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EDITION



## I A

1	1s <sup>1</sup>
<b>H</b>	
1.0080	

## II A

3	(He) 2s <sup>1</sup>	4	(He) 2s <sup>2</sup>
<b>Li</b>		<b>Be</b>	
6.939		9.012	

11	(Ne) 3s <sup>1</sup>	12	(Ne) 3s <sup>2</sup>
<b>Na</b>		<b>Mg</b>	
22.99		24.31	

## III B IV B V B VI B VII B

19	(Ar) 4s <sup>1</sup>	20	(Ar) 4s <sup>2</sup>	21	(Ar) 3d <sup>1</sup> 4s <sup>2</sup>	22	(Ar) 3d <sup>2</sup> 4s <sup>2</sup>	23	(Ar) 3d <sup>3</sup> 4s <sup>2</sup>	24	(Ar) 3d <sup>5</sup> 4s <sup>1</sup>	25	(Ar) 3d <sup>5</sup> 4s <sup>2</sup>	26	(Ar) 3d <sup>6</sup> 4s <sup>2</sup>	27	(Ar) 3d <sup>7</sup> 4s <sup>2</sup>
<b>K</b>		<b>Ca</b>		<b>Sc</b>		<b>Ti</b>		<b>V</b>		<b>Cr</b>		<b>Mn</b>		<b>Fe</b>		<b>Co</b>	
39.102		40.08		44.96		47.90		50.94		52.00		54.94		55.85		58.93	

37	(Kr) 5s <sup>1</sup>	38	(Kr) 5s <sup>2</sup>	39	(Kr) 4d <sup>1</sup> 5s <sup>2</sup>	40	(Kr) 4d <sup>2</sup> 5s <sup>2</sup>	41	(Kr) 4d <sup>3</sup> 5s <sup>1</sup>	42	(Kr) 4d <sup>4</sup> 5s <sup>1</sup>	43	(Kr) 4d <sup>5</sup> 5s <sup>2</sup>	44	(Kr) 4d <sup>6</sup> 5s <sup>1</sup>	45	(Kr) 4d <sup>7</sup> 5s <sup>1</sup>
<b>Rb</b>		<b>Sr</b>		<b>Y</b>		<b>Zr</b>		<b>Nb</b>		<b>Mo</b>		<b>Tc</b>		<b>Ru</b>		<b>Rh</b>	
85.47		87.62		88.90		91.22		92.91		95.94		(99)*		101.07		102.90	

55	(Xe) 6s <sup>1</sup>	56	(Xe) 6s <sup>2</sup>	57	(Xe) 5d <sup>1</sup> 6s <sup>2</sup>	72	(Xe) 4f <sup>14</sup> 5d <sup>2</sup> 6s <sup>2</sup>	73	(Xe) 4f <sup>14</sup> 5d <sup>3</sup> 6s <sup>2</sup>	74	(Xe) 4f <sup>14</sup> 5d <sup>4</sup> 6s <sup>2</sup>	75	(Xe) 4f <sup>14</sup> 5d <sup>5</sup> 6s <sup>2</sup>	76	(Xe) 4f <sup>14</sup> 5d <sup>6</sup> 6s <sup>2</sup>	77	(Xe) 4f <sup>14</sup> 5d <sup>7</sup> 6s <sup>2</sup>
Cs		Ba		La <sup>*</sup>		Hf		Ta		W		Re		Os		Ir	
132.90		137.34		138.91		178.49		180.95		183.85		186.2		190.2		192.2	

87	(Rn) 7s <sup>1</sup>	88	(Rn) 7s <sup>2</sup>	89	(Rn) 6d <sup>1</sup> 7s <sup>2</sup>	104	(Rn) 5f <sup>14</sup> 6d <sup>2</sup> 7s <sup>2</sup>
<b>Fr</b>		<b>Ra</b>		<b>Ac†</b>		<b>?</b>	
(223)		(226)		(227)			

Color key: Gray symbol denotes gaseous element; blue, liquid element; and black, solid element.

\* Lanthanide Series

58	(Xe) 4f <sup>2</sup> 6s <sup>2</sup>	59	(Xe) 4f <sup>3</sup> 6s <sup>2</sup>	60	(Xe) 4f <sup>4</sup> 6s <sup>2</sup>	61	(Xe) 4f <sup>5</sup> 6s <sup>2</sup>	62	(Xe) 4f <sup>6</sup> 6s <sup>2</sup>	63	(Xe) 4f <sup>7</sup> 6s <sup>2</sup>
Ce		Pr		Nd		Pm		Sm		Eu	
140.12		140.91		144.24		(147)		150.35		151.96	

† Actinide Series

90	(Rn) 6d <sup>2</sup> 7s <sup>2</sup>	91	(Rn) 5f <sup>2</sup> 6d <sup>1</sup> 7s <sup>2</sup>	92	(Rn) 5f <sup>3</sup> 6d <sup>1</sup> 7s <sup>2</sup>	93	(Rn) 5f <sup>4</sup> 6d <sup>1</sup> 7s <sup>2</sup>	94	(Rn) 5f <sup>5</sup> 7s <sup>2</sup>	95	(Rn) 5f <sup>6</sup> 7s <sup>2</sup>
<b>Th</b>		<b>Pa</b>		<b>U</b>		<b>Np</b>		<b>Pu</b>		<b>Am</b>	
232.04		(231)		238.03		(237)		(244)		(243)	

## VIII A

2	1s <sup>2</sup>
<b>He</b>	
4.0026	

## III A IV A V A VI A VII A

5	(He) 2s <sup>2</sup> 2p <sup>1</sup>	6	(He) 2s <sup>2</sup> 2p <sup>2</sup>	7	(He) 2s <sup>2</sup> 2p <sup>3</sup>	8	(He) 2s <sup>2</sup> 2p <sup>4</sup>	9	(He) 2s <sup>2</sup> 2p <sup>5</sup>	10	(He) 2s <sup>2</sup> 2p <sup>6</sup>
<b>B</b>		<b>C</b>		<b>N</b>		<b>O</b>		<b>F</b>		<b>Ne</b>	
10.81		12.011		14.007		15.999		18.998		20.183	

13	(Ne) 3s <sup>2</sup> 3p <sup>1</sup>	14	(Ne) 3s <sup>2</sup> 3p <sup>2</sup>	15	(Ne) 3s <sup>2</sup> 3p <sup>3</sup>	16	(Ne) 3s <sup>2</sup> 3p <sup>4</sup>	17	(Ne) 3s <sup>2</sup> 3p <sup>5</sup>	18	(Ne) 3s <sup>2</sup> 3p <sup>6</sup>
<b>Al</b>		<b>Si</b>		<b>P</b>		<b>S</b>		<b>Cl</b>		<b>Ar</b>	
26.98		28.09		30.974		32.06		35.453		39.948	

## I B II B

28	(Ar) 3d <sup>8</sup> 4s <sup>2</sup>	29	(Ar) 3d <sup>9</sup> 4s <sup>1</sup>	30	(Ar) 3d <sup>10</sup> 4s <sup>2</sup>	31	(Ar) 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>1</sup>	32	(Ar) 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>2</sup>	33	(Ar) 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>3</sup>	34	(Ar) 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>4</sup>	35	(Ar) 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>5</sup>	36	(Ar) 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>6</sup>
Ni		Cu		Zn		Ga		Ge		As		Se		Br		Kr	
58.71		63.54		65.37		69.72		72.59		74.92		78.96		79.909		83.80	

46	(Kr) 4d <sup>10</sup>	47	(Kr) 4d <sup>10</sup> 5s <sup>1</sup>	48	(Kr) 4d <sup>10</sup> 5s <sup>2</sup>	49	(Kr) 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>1</sup>	50	(Kr) 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>2</sup>	51	(Kr) 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>3</sup>	52	(Kr) 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>4</sup>	53	(Kr) 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>5</sup>	54	(Kr) 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>6</sup>
<b>Pd</b>		<b>Ag</b>		<b>Cd</b>		<b>In</b>		<b>Sn</b>		<b>Sb</b>		<b>Te</b>		<b>I</b>		<b>Xe</b>	
106.4		107.87		112.40		114.82		118.69		121.75		127.60		126.90		131.30	

78	(Xe) 4f <sup>14</sup> 5d <sup>9</sup> 6s <sup>1</sup>	79	(Xe) 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>1</sup>	80	(Xe) 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>	81	(Xe) 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>1</sup>	82	(Xe) 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>	83	(Xe) 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>3</sup>	84	(Xe) 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>4</sup>	85	(Xe) 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>5</sup>	86	(Xe) 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>6</sup>
<b>Pt</b>		<b>Au</b>		<b>Hg</b>		<b>Tl</b>		<b>Pb</b>		<b>Bi</b>		<b>Po</b>		<b>At</b>		<b>Rn</b>	
195.09		196.97		200.59		204.37		207.19		208.98		(210)		(210)		(222)	

In several cases, atomic weight is rounded to four or five significant figures. See inside back cover for listing of 1961 International Atomic Weights. Electron configurations taken from *Theoretical Inorganic Chemistry* by M. Clyde Day and Joel Selbin, Reinhold Publishing Corporation, except number 104, which is predicted by analogy.

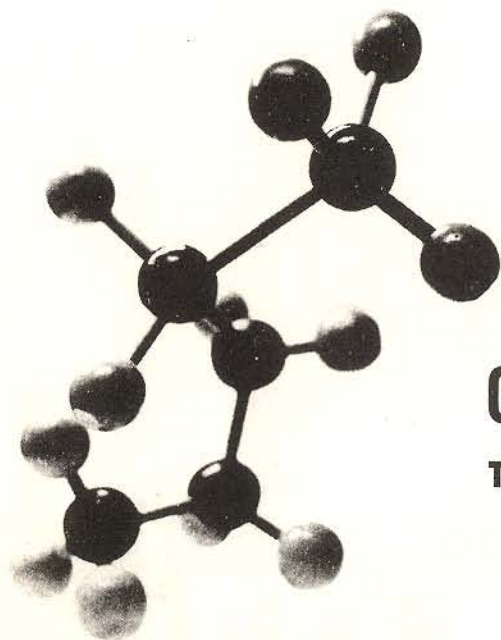
\*Value in parentheses denotes mass number of most stable known isotope.

†Name and symbol are not officially accepted. See page 375.

64	(Xe) 4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>	65	(Xe) 4f <sup>9</sup> 6s <sup>2</sup>	66	(Xe) 4f <sup>10</sup> 6s <sup>2</sup>	67	(Xe) 4f <sup>11</sup> 6s <sup>2</sup>	68	(Xe) 4f <sup>12</sup> 6s <sup>2</sup>	69	(Xe) 4f <sup>13</sup> 6s <sup>2</sup>	70	(Xe) 4f <sup>14</sup> 6s <sup>2</sup>	71	(Xe) 4f <sup>14</sup> 5d <sup>1</sup> 6s <sup>2</sup>
<b>Gd</b>		<b>Tb</b>		<b>Dy</b>		<b>Ho</b>		<b>Er</b>		<b>Tm</b>		<b>Yb</b>		<b>Lu</b>	
157.25		158.92		162.50		164.93		167.26		168.93		173.04		174.97	

96	(Rn) 5f <sup>7</sup> 6d <sup>1</sup> 7s <sup>2</sup>	97	(Rn) 5f <sup>8</sup> 6d <sup>1</sup> 7s <sup>2</sup>	98	(Rn) 5f <sup>10</sup> 7s <sup>2</sup>	99	(Rn) 5f <sup>11</sup> 7s <sup>2</sup>	100	(Rn) 5f <sup>12</sup> 7s <sup>2</sup>	101	(Rn) 5f <sup>13</sup> 7s <sup>2</sup>	102	(Rn) 5f <sup>14</sup> 7s <sup>2</sup>	103	(Rn) 5f <sup>14</sup> 6d <sup>1</sup> 7s <sup>2</sup>
<b>Cm</b>		<b>Bk</b>		<b>Cf</b>		<b>Es</b>		<b>Fm</b>		<b>Md</b>		<b>No<sup>b</sup></b>		<b>Lr</b>	
(247)		(247)		(249)		(254)		(253)		(256)		(256)		(257)	





# GENERAL

## THIRD EDITION

**A HARPER INTERNATIONAL EDITION**

Jointly published by

**HARPER & ROW**, New York, Evanston & London  
and **JOHN WEATHERHILL, INC.**, Tokyo

# COLLEGE CHEMISTRY

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The University of Tennessee

**JESSE H. WOOD**

Professor of Chemistry  
The University of Tennessee

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## PREFACE TO THE THIRD EDITION

The accelerating activities of the chemical profession and the attendant recent developments in theory and technology make this an ideal time for revising a text in beginning college chemistry. Of even greater importance is the opportunity today to build on the innovations in the teaching of chemistry that have been introduced in this decade in both high schools and colleges, innovations that have resulted from the leadership and enthusiasm of so many chemists in and out of the teaching profession.

The continuing growth in the basic subject matter, coupled with the pressure to include, in the introductory course, topics formerly in advanced courses, has long been a problem for every teacher (and every student!) of general chemistry. This text is offered as a solution to that problem as it relates to the thorough chemistry course designed for liberal arts and professional students. Our philosophy has been to maintain the breadth of coverage of the previous editions, but, by paring away dated material and by changes in emphasis, to achieve more fundamental treatments of concepts such as structure, energy relationships, and reaction mechanisms. This complete revision has involved every chapter; the exercises are essentially new, only a few particularly useful ones having been retained.

In keeping with the purpose of a text designed for the student who may or may not go on to take further chemistry courses, we have brought the chapters on nuclear chemistry, organic chemistry, and the chemical nature of our world up to date and have introduced a section on spectroscopy, a subject that is of great importance to modern chemistry. Further features of this revision are a fuller and earlier study of atomic theory, the introduction of orbitals when chemical bonding is first taken up, the use of orbital theory later in both inorganic and organic discussions, a systematic development of thermochemistry, and the correlation of descriptive organic chemistry with concepts of structure and mechanism. Descriptive inorganic chemistry has not been slighted. It appears that, with an increasing accent on theory from high school courses onward, the role of general chemistry in presenting a core of factual data is becoming more important. Many industrial and commercial applications have been included to illustrate the great practical importance of chemistry to our society.

One aim of this text is to recognize that the preparation of the average student entering college is improving. Although we do not assume that every student has had a full year of high school chemistry, we do expect that he has had either chemistry or physics and that his high school mathematics has given him facility in arithmetical and simple algebraic calculations. For the student who wishes to review certain mathematical techniques useful in solving

chemistry problems, there are illustrative sections in the Appendix. Relationships that require calculus have not been introduced. So far as thermodynamics and kinetics are concerned, the aim of the text is to lead the student, on the one hand, to an understanding of introductory quantitative thermochemistry and the related notions of thermochemical cycles, enthalpy, and entropy, and, on the other hand, to an understanding of how rates of reaction are related to equilibrium and mechanism. For a course in general chemistry these are lofty objectives.

Some economy in presentation has resulted from the reorganization of the first quarter of the text and from not presenting the history of chemistry and methods of scientific discovery in separate chapters. These important subjects have not been neglected, for a few selected historical topics have been developed in some depth to show, by example, aspects of scientific methods. The unfolding of theories of atomic structure, the determination of atomic weight, the discovery of nuclear fission, and the chemical evidence for isomers are instances of this case-history approach.

Throughout we have endeavored to use systematic nomenclature and symbols, relying principally on the recommendations of *Chemical Abstracts* and the *Journal of the American Chemical Society*, except that we have followed the increasingly accepted style of writing abbreviations without periods. Again, we have provided lists of supplementary readings where appropriate. These were chosen in part to acknowledge those references which we found most helpful and in part to suggest sources of further information to student and teacher. A systematic survey of pertinent articles was restricted to recent issues of the *Journal of Chemical Education* and to *Scientific American* on the ground that these are readily available to students.

Finally, we must express our gratitude to those who have helped us so generously. To write a book of such broad coverage would not have been possible for us without the continuing support of our fellow staff members at the University of Tennessee. Repeated assistance was given by Drs. N. S. Bowman, W. E. Bull, J. A. Dean, W. H. Fletcher, A. D. Melaven, T. P. Salo, A. F. Saturno, G. K. Schweitzer, and W. T. Smith. Particularly helpful among the suggestions from members of other faculties were those of Drs. D. M. Agar and J. N. Agar of Cambridge University and Dr. F. L. James of Miami University. In producing the book a great share of the burden was born by Mrs. Georgia Troglen, our peerless typist, and by our wives, who, we trust, have almost come to enjoy their editing and proofreading. We hope that all who had a part in bringing out this book share our pleasure with the result. And we hope each student finds pleasure and interest in the presentation to help lighten his labors.

CHARLES W. KEENAN  
JESSE H. WOOD



## PREFACE TO THE SECOND EDITION

Underlying this presentation of a first college course in chemistry is the belief that the study of chemistry can make a worthwhile contribution to the education of any student. Concerned as it is with fundamental concepts about our environment and with the applications of these concepts in controlling our environment, chemistry is a legitimate part of a cultural education.

The authors are convinced that general chemistry most adequately serves the student's needs with respect to later specialization and helps best to give him the stamp of an educated man when it is patterned as a liberal arts course with the aim of developing fundamental principles in the major fields of chemistry. No great difference in content is necessary for students with differing professional interests. Since chemistry is concerned with changes in the structure and properties of matter, such a course logically begins with the fundamental particles of matter and proceeds to show how these are organized to form all the substances about us. A sufficient amount of descriptive subject matter is introduced to support the logical development of unifying principles and theories. As the student's understanding of the structure of matter is extended, applications in the broad areas touching his life are made. The linking together of these seemingly different phases of chemistry through a few fundamental laws and theories can be fascinating though rigorous for the student.

This book, then, is written from the point of view that general college chemistry should be a course which permits specialization in any field (including chemistry) that the student may choose later. For this reason, structural chemistry, nuclear chemistry, geochemistry, organic chemistry, and biochemistry are covered perhaps somewhat more than is customary. The amount of subject matter presented in the fields of inorganic and metallurgical chemistry is probably less than in most texts, not because these are less important but because they are not more important than other fields to the beginning student.

Another objective is to present a book that can be read and understood by college freshmen of average preparation and intelligence. Our experience confirms the opinions of others: that many students entering colleges and universities are poorly prepared for a rigorous course in college chemistry.

The major changes in this revised edition have been made with the advice and cooperation of colleagues in other institutions who used the first edition. On the basis of their suggestions and of our own familiarity with the text, we have made some additions, a few deletions, and some important changes in the order of presentation.

A brief treatment of atomic orbitals has been included. Some

material on nuclear chemistry has been added, but this subject is now presented in two chapters—one more concerned with fundamental principles, the other with applications—in order that part of this material may be omitted more easily if the instructor does not have adequate time to cover it. The discussion on ionic equilibria has been expanded somewhat. Other changes include the introduction of the periodic table and details of atomic structure at an earlier point and the addition of timely topics here and there. A number of thought-provoking and more complex problems have been added to the exercises; answers to perhaps one-third of the problems have been omitted.

We wish to express our deep appreciation for the generous help of our friends in other institutions who responded to our questionnaire or who took the time to write us letters offering suggestions. We also take pleasure in acknowledging the contributions of our colleagues at The University of Tennessee. Mr. Sidney Snelson has again prepared the drawings and has made this part of our job a pleasure rather than a task. Miss Dorothy Thompson of Harper & Brothers has continued to edit our work, managing somehow always to make the finished sentence what we had hoped for in the original. Finally, our appreciation to two authors' wives for their editing, proofreading, and constant encouragement.

C. W. KEENAN  
J. H. WOOD

*Knoxville, Tennessee*



Bear in mind that the wonderful things you learn in your schools are the work of many generations, produced by enthusiastic effort and infinite labor in every country of the world. All this is put into your hands as your inheritance in order that you may receive it, honor it, add to it, and one day faithfully hand it on to your children. Thus do we mortals achieve immortality in the permanent things which we create in common.

—Albert Einstein



**CHEMICAL****CONCEPTS; SCIENTIFIC****MEASUREMENTS**

*Introduction.* Throughout history man has been fascinated by the study of nature, by the study of his world and his place in it. Among the works of man which have lived longest and which have been revered most have been those concerned with nature. During the past twenty-five centuries, an inspiring record of this search for understanding has been compiled, of questions and answers about the earth and its creatures and the enveloping universe.

Early in the development of Western culture, many fundamental questions about and explanations of natural phenomena were collected and developed with great insight by Greek philosophers living about 500 to 300 B.C. Among the questions that these thinkers pondered were: What are the simplest kinds of matter? Why does an object like a rock fall, whereas fire rises? Is the earth flat or round? Can matter be created or destroyed, or can it merely change in form? Is it possible for living creatures to be generated from nonliving matter? Did land animals develop from fishes that crawled out of the sea? How are the characteristics of a father and mother passed on to their children?

Although some of these questions have been answered, after twenty-five centuries we are still intrigued by many of the same puzzles. From the earliest times, answers to questions about nature have been sought in two general ways. One way is by pure thought and logical argument, the method of *rationalism*. The other is by gathering facts and making observations, the method of *empiricism*. In science, neither of these methods is wholly independent of the other: one must have some facts before he can rationalize; and one must be logical and rational if he is to interpret his empirical observations. Yet, in a given situation, one method can be emphasized more than the other.



In the time of the Greeks and for more than twenty centuries afterward, rationalism was the method emphasized in the study of natural phenomena. In Western Europe from about 1100 to 1500 rationalism was not only emphasized, but the belief was widely held that the ancient Greek rationalizations were the most nearly perfect. In the Middle Ages, the philosophers of nature studied ancient texts and logical arguments more avidly than they studied nature itself. It was not until the sixteenth or seventeenth century that empirical methods began to be relied on heavily and that science as we know it today began to be practiced.

The scientific awakening in Western culture occurred roughly between 1500 and 1700. Certainly prior to 1500 there were men of a scientific frame of mind, just as since 1700 there have been non-scientific ones, but during these centuries science (and empiricism) began its climb toward a dominant philosophic position in our culture.

Empiricism is intimately related to the experimental method of testing our ideas. As an example, consider the ancient idea that everything is made of water. Jan Baptista von Helmont, in the sixteenth century, was one of those who were not satisfied with the age-old rational argument, based on casual observations, that plants were composed almost entirely of water. In an experiment similar to one by Nicolas of Cusa of over a century earlier, von Helmont planted a young willow tree in a tub of earth and added nothing but water to the tub over a long period. In five years the tree gained 164 lb, an increase in weight, von Helmont concluded, that must have been due to the water being changed in form to "tree substance." But it took many years and many more empirical tests before it was possible to account for the increase in weight of a plant mainly in terms of three substances—hydrogen, oxygen, and carbon. As we shall see in our study of the chemistry of photosynthesis, the chemist today has a rather detailed explanation of the gain in weight of the willow tree based on countless observations and measurements.

Chemistry is the rational and empirical study of the structure of matter and the changes that matter undergoes in natural processes and in planned experiments. In chemistry, as in all natural sciences, we rely on empirical tests of our ideas; and, as in all sciences, we focus our attention on *reproducible* facts, that is, on events or occurrences that take place in the same way when all conditions are the same. Most of the phenomena and materials of nature appear to us to be strictly reproducible. The burning of 1 lb of carbon produces a given amount of energy. Water freezes whenever its temperature drops to 32°F. Carbohydrates are oxidized in the tissues of animals to carbon dioxide and water.

During the past two or three centuries, the chemist has collected an immense number of reproducible facts. Whenever possible, as he searches for order in his growing collection, the scientist summarizes a number of facts in a concise statement that he calls a *law* (or a

law of nature). The scientist is usually interested in the rational explanation of his facts and laws by means of a hypothesis or a theory designed to suggest why or how something happens as it does. In the language of science, a hypothesis is similar to a theory but is usually less formal and is based on a less thorough study.

It is not possible, indeed not desirable, to separate the facts, laws, and theories of chemistry from those of other sciences. The arbitrary divisions of natural studies into physics, astronomy, geology, botany, zoology, chemistry, and other sciences are not classifications imposed by nature, but by man. Chemistry draws heavily on all the sciences for helpful ideas, and it contributes to many areas in all other sciences. Chemistry has been called the *servant science*, because it supplies descriptions and understanding of the many kinds of matter that are studied in detail in other sciences. Whether a student is interested in medicine, meteorology, home economics, agriculture, or one of the fields of engineering, he will often find that chemical facts and theories are of great importance to him. For the nonscientist, a study of chemistry enriches his understanding of the world of nature and of the somewhat unnatural world of new materials that the chemical industry provides for him.

## CHEMICAL DESCRIPTION OF MATTER

### PROPERTIES

Every substance—for example, water, sugar, salt, silver, or copper—has a set of characteristics or properties that distinguish it from all other substances and give it a unique identity. Both sugar and salt are white, solid, crystalline, soluble in water, and odorless. But the former has a sweet taste, melts and turns brown on heating in a saucepan, and burns in air. The latter tastes salty, does not melt till heated above red heat, does not turn brown no matter how high it is heated, and does not burn in air, although it gives off a bright yellow light when heated in a flame. We have described both of these substances by listing some of their respective intrinsic properties.

*Intrinsic properties* are qualities that are characteristic of any sample of a substance, regardless of the shape or size of the sample. *Extrinsic properties* are qualities that are not characteristic of the substance itself. Size, shape, length, weight, and temperature are extrinsic properties.

*Physical Properties.* A number of intrinsic properties are especially useful in describing materials. One group of these includes taste, odor, color, and transparency. The qualities in this group are common enough, but it is difficult to assign definite values to them expressed in numbers. A second group of intrinsic properties includes melting point, boiling point, density, viscosity, refractive index, and

## CHEMICAL CONCEPTS; SCIENTIFIC MEASUREMENTS

hardness. The qualities in this group can be measured easily and expressed in definite numbers. The substance that we call grain alcohol melts at  $-114.6^{\circ}\text{C}$  ( $-174.3^{\circ}\text{F}$ ), boils at  $78.3^{\circ}\text{C}$  ( $173^{\circ}\text{F}$ ), has a density of 0.785 g/ml, and a refractive index of 1.3624. No other substance has precisely this set of unique properties; such a substance is grain alcohol and nothing else.

Intrinsic properties of the type that we have been discussing (color, odor, taste, melting point, density, etc.) are commonly referred to as *physical properties*.

*Chemical Properties.* The tendency of a substance to change, either alone or by interaction with other substances, and in so doing to form different materials involves a second class of intrinsic properties. For example, it is characteristic of alcohol to burn, of iron to rust, of wood to decay. These characteristics are referred to as *chemical properties*.

## CHANGES IN MATTER AND ENERGY

*Changes in Matter.* The materials around us are subject to constant change. Plant and animal materials decay, metals corrode, water changes to ice when the temperature drops sufficiently and changes back to the liquid form when the temperature rises, land areas erode, and lakes and seas evaporate. When we study these changes, we find we can classify them under two headings: chemical change and physical change. **Chemical changes** are those which result in the disappearance of substances and the formation of new ones. For example, when pieces of magnesium metal burn in a photo-flash bulb, the magnesium and some oxygen from the bulb disappear. In their place, we find a powdery, incombustible solid, magnesium oxide, that has its own unique set of properties. Or, as another example, consider some of the changes in matter that occur as a stalk of corn matures. In this process, carbon dioxide and water disappear in the sense that they are converted to glucose sugar in the growing plant. Much of this sugar accumulates in the ear of the corn, and as the ear matures, the sugar is converted to starch. The glucose sugar that appears has its own set of identifying properties that are completely different from the carbon dioxide and water from which it was made. The starch, in turn, has different properties from the sugar. Chemical changes are also referred to as *chemical reactions*.

The second type of change, **physical change**, is that which does not result in the formation of new substances. For example, when ice melts to water, or when sand is ground to a fine powder, no new substance is formed. However, it should be noted that in physical changes some properties do change and energy transformations do occur.

**Changes in Energy.** Every change, chemical or physical, involves energy, the ability to do work. The energy of a body or a system is that body's or system's ability to do work. The flight of a bird, the breaking of the earth's crust by a new blade of grass, the burning of wood, the turning of a page in a book—all these actions involve energy.

There are a number of varieties of energy. *Heat energy, electrical energy, potential energy, kinetic energy, radiant energy, chemical energy, and atomic energy* are common types. One type of energy can be converted into any other type.

The **heat energy** of a body is a measure of the internal energy of a substance that is due to its temperature. Heat energy can be transferred from one body to another either by radiation or by conduction (actual contact).

**Potential energy** may be thought of as the energy that a body possesses because of its position or because of its existence in a state other than its state of lowest energy. The water held in a reservoir behind a dam is in a position to do work by turning a turbine or water wheel and hence possesses potential energy. A tightly wound watch spring also possesses potential energy. As the water flows through turbines or the watch spring slowly uncoils, potential energy is transformed to **kinetic energy**, the energy that a body possesses by virtue of its motion. A moving automobile, a pitched baseball, an airplane in flight—all possess kinetic energy.

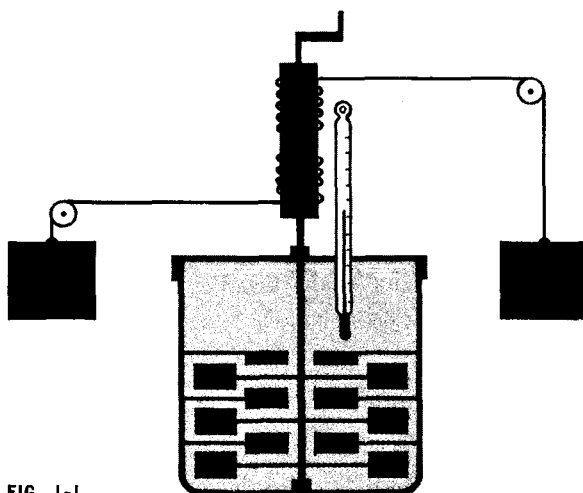
Kinetic energy depends on both mass and velocity. A change in the velocity of a moving body has a greater effect on its kinetic energy than does a proportionate change in its mass, because the kinetic energy is proportional to the square of the velocity. To illustrate, three identical automobiles, one moving at 20, one at 40, and one at 60 mph, have kinetic energies in the ratio of 1:4:9, that is,  $1:2^2:3^2$ . It would require nine times as much work to bring the one moving at 60 mph to a stop as is required for the one moving at 20 mph. But if the mass were tripled and the velocity not changed, the kinetic energy would be increased by just three times. That is, the kinetic energy is directly proportional to the mass. The dependence of kinetic energy on mass and velocity is summed up in the expression

$$KE = \frac{1}{2}mv^2$$

**Radiant energy** is the type of energy associated with ordinary light, X rays, radio waves, or infrared rays. Radiant energy is also called electromagnetic radiation. All such radiation travels through space with the speed of light (186,000 miles/sec).

Frequently, the energy in coal, gasoline, dynamite, food, or an automobile battery is referred to as potential energy. This type of energy is more appropriately called **chemical energy**. Chemical energy is transformed to other kinds of energy when matter undergoes the





The potential energy of the weights is transformed into heat energy by the friction between the rotating paddle wheel and water. The rise in the temperature of the water gives data for calculating the mechanical equivalent of heat:  $1 \text{ ft lb} = 0.324 \text{ cal}$ .

FIG. 1-1

proper kind of change. For example, when coal and gasoline burn, or when the food we eat is "burned" in our cells, chemical energy is converted to heat or light energy or both. Conversely, other kinds of energy can be transformed to chemical energy by the proper kind of change. Radiant energy from the sun is transformed in a growing corn plant to chemical energy that becomes associated with the substances making up the stalk, corn grains, and other parts of the plant. All life processes involve the change of chemical energy to other forms of energy. Chemical energy is the principal source of energy for all the needs of our factories, our homes, our transportation, and other activities.

A kind of energy called **atomic energy** or **nuclear energy** is associated with the manner in which atoms are constructed. Methods for transforming this type of energy to heat, light, and other kinds of energy have been developed in our generation. Atomic energy is discussed in detail in Chap. 14.

An illustration of the transformation of potential energy to heat energy is shown in Fig. 1-1.

**Exothermic and Endothermic Changes.** As a result of every physical or chemical change, there is a change in energy. If substances, or a single substance, change in such a way that energy is given to the surroundings, the change is said to be **exothermic** (heat comes out). The combining form *-thermic* originally referred to heat energy, but exothermic now refers to a change in which any type of energy is given off.

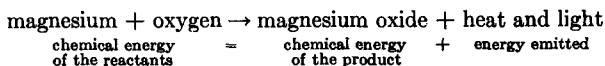
For example, when magnesium burns in oxygen to make magnesium oxide, chemical energy is converted to heat and light energy that is emitted to the surroundings. This is an exothermic chemical

change. Or when a hot bowl loses heat to the table on which it has been placed, the cooling of the bowl is an exothermic physical change.

When carbon dioxide and water are changed to glucose in a growing plant, radiant energy from the sun is converted to chemical energy. Such a change in which materials take up energy from the surroundings is said to be **endothermic**. This formation of glucose is an endothermic chemical reaction. In the example of the hot bowl on the table, mentioned previously, the taking up of heat by the table is an endothermic physical change. For the bowl the change is exothermic, but for the table the change is endothermic.

A process that is exothermic in one direction is always endothermic in the opposite direction, and vice versa. The reaction of magnesium and oxygen to form magnesium oxide is exothermic, whereas the breaking down of magnesium oxide to yield magnesium and oxygen is an endothermic change. In fact, the amount of energy required to break down a given amount of magnesium oxide is equal to the amount of energy given off when that much magnesium oxide is formed.

*Energy is neither created nor destroyed in any transformation of matter.* This statement, the **law of conservation of energy**, seems to describe all natural phenomena accurately, whether in the field of chemistry, physics, biology, geology, astronomy, or any other. Consider the following example:



If no energy is created or destroyed, the total energy of the system before the reaction equals the energy after the reaction. In this reaction, therefore, the chemical energy of the product must be less than the chemical energy of the reactants, because some chemical energy is transformed to heat and light during the reaction. In any endothermic reaction, just the reverse would be true: the chemical energy of the products would be greater than the chemical energy of the reactants.

## SCIENTIFIC MEASUREMENTS

### METRIC SYSTEM

One of the hurdles the American student of science must clear is the learning of a new system of weights and measures. In the United States the units of measure used in everyday life are those of the English system. People in the countries of Western Europe use the metric system. The metric system is employed universally in scientific work. A young Frenchman or Russian or Italian uses the same system in his everyday life that he does in studying science. He runs in the 100-meter dash, he drinks a liter of milk a day, and he goes

## CHEMICAL CONCEPTS; SCIENTIFIC MEASUREMENTS

with a girl who weighs about 50 kilograms. If he expected the temperature outside to be  $35^{\circ}$ , he would not wear a sweater or a coat, for he would think of the temperature on the centigrade scale, where a reading of  $35^{\circ}$  is equivalent to  $95^{\circ}$  Fahrenheit—a hot day (see Fig. 1-2).

The basic measurements of chemistry, or any science, include these:

How long?	What is the distance between two points?
How much surface?	What is the area of a body?
How big?	How much space or volume does an object take up?
How heavy?	What is the mass (or weight) of a body?
How long in time?	How is time measured?
How hot?	How is temperature measured?
How energetic?	How much work can be obtained from a process or an action? In what units is energy measured?

The metric system of measurements will generally be employed in this book, although a familiarity with the English system is assumed also. In Table 1 of the Appendix some common relationships between these two systems are listed. At the end of this chapter there are a number of exercises that are designed to provide practice in doing calculations with scientific units of measure. Also in the Appendix there is a description of the *factor-units method* of doing calculations and a brief description of the use of *exponents*. If you are unfamiliar with these arithmetical procedures, you should begin at once to study them, for they will be of use throughout your study of chemistry.

A mention of the arbitrary choice of standards of measurement is in order. Consider length. At different times and in different places many standards of length have been used. A thumb's width was called an inch in ancient Scotland, and the king went so far as to define an inch as the average width of three thumbs—one of a large, one of a medium, and one of a small man. In England the inch was once defined as the length of four barleycorns, at another time as three. The foot was often related to the length of a man's foot, but in different places a unit of this name represented the equivalent of 10, 12, 13, 17, or even 27 modern inches. Half a dozen versions have been used in the same country at the same time; a merchant might use one measure when buying, another when selling.

The choices of the scientific units of measure are just as arbitrary as any of the foregoing, but in science an effort has been made to choose a unit that can be *precisely* and *reproducibly* measured. The basic metric unit of length, and therefore of area and volume, is the meter. It was originally defined by the French Academy of Science as one ten-millionth of the distance from the North Pole to the equator. The distance from the pole to the equator was precisely measured by astronomers, and then the length corresponding to

A comparison of the centigrade and Fahrenheit temperature scales.

$$\begin{aligned} 100^{\circ} - 0^{\circ} &= 100 \text{ centigrade units} \\ 212^{\circ} - 32^{\circ} &= 180 \text{ Fahrenheit units} \\ \frac{100}{180} &= \frac{5}{9} \\ ^{\circ}\text{C} &= (^{\circ}\text{F} - 32^{\circ}) \frac{5}{9} \\ ^{\circ}\text{F} &= ^{\circ}\text{C} \left( \frac{9}{5} \right) + 32^{\circ} \end{aligned}$$

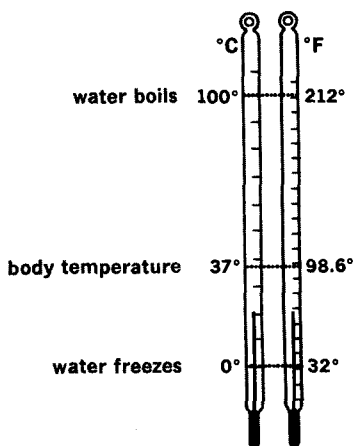


FIG. 1-2

1/10,000,000 of this was carefully marked off on a bar of platinum-iridium alloy. This bar, the standard meter, is kept at nearly constant temperature at the International Bureau of Weights and Measures just outside Paris, and other standards, for use around the world, are compared with it. (There is a more recent definition of the meter mentioned in Table 3-1.) In laboratory work the centimeter (1/100 meter) is often the most convenient unit of length.

## USE OF WATER AS STANDARD OF COMPARISON

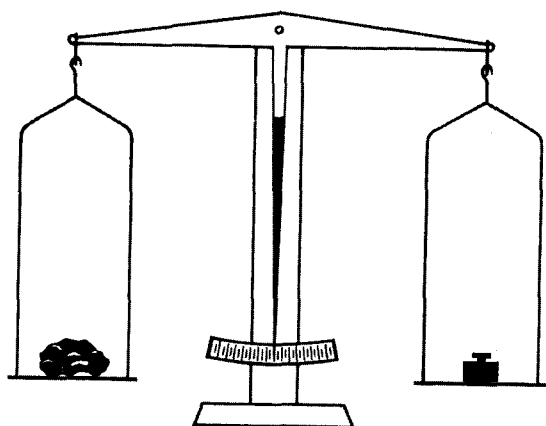
For many important measurements the properties of water are taken as arbitrary standards. The standard of mass was originally chosen so that one cubic centimeter (cc) of water at 4°C would have a mass of one gram (g). The standard mass was defined as the mass of 1,000 cc of water at 4°C and was called the kilogram. A piece of platinum of precisely this mass was placed in the International Bureau of Weights and Measures. It was found later, by more precise methods, that the piece of platinum so carefully made did not have the same mass as 1,000 cc of water. It was decided to keep the standard kilogram as it was to avoid having to change the standard weights the world over. Therefore, the **gram** is defined as one-thousandth of the standard kilogram. The U.S. Bureau of Standards is the custodian of the standard kilogram weight in the United States.

Strictly speaking, mass and weight are different units. **Mass** refers to the quantity of matter in a body, whereas **weight** refers to the gravitational attraction of the earth for a body (see Fig. 1-3).

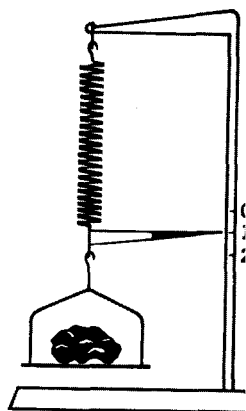
The size of an object can be expressed in terms of cubic centimeters. It can also be expressed in terms of liters. By definition, a **liter** is the volume of a kilogram (kg) of water at 4°C. One cubic



## CHEMICAL CONCEPTS; SCIENTIFIC MEASUREMENTS



equal-arm balance



spring scale

FIG. 1-3

The mass of the object on the left pan of the balance is equal to the defined mass of the standard on the right pan; the deflection of the pointer does not change with a change in gravity. The deflection of the pointer of the spring scale is subject to some variation from place to place on the earth's surface due to gravitational changes.

centimeter is a tiny bit smaller than 1 milliliter (ml), but for most measurements the two may be considered identical. (One liter equals 1,000.000 ml equals 1,000.028 cc, or 1.000000 ml equals 1.000028 cc.)

Volumes of materials used in the laboratory are usually expressed in terms of milliliters, although the cubic centimeter is often employed. These units are commonly used interchangeably, because they are so very nearly equal.

The fact that water is the standard substance for defining units of mass and volume means that its density is precisely unity also. The density of a substance is its mass per unit volume, and the density of water at 4°C (the temperature of its maximum density) is precisely one gram per milliliter. An object with a density greater than 1 g/ml will sink in water; an object with a density less than 1 g/ml will float. Densities of some common substances are given in Table 1-1.

Water is also the standard substance used for defining the temperature scale. The difference in temperature between normal freezing point and boiling point is arbitrarily divided into 100 graduations, and so the scale is called the **centigrade scale**. The normal freezing point of water is defined as 0°C, and the normal boiling point as 100°C. Because the Swedish astronomer Anders Celsius developed this scale (in 1742), many persons prefer to call it the **Celsius scale** rather than the centigrade scale. In either case the symbol C is used.

The common unit of heat energy is the **calorie**, which is defined as the heat energy necessary to change the temperature of 1 g of water by 1°C (from 15 to 16°C for the precise definition). To measure

any type of energy, the chemist often converts it to heat energy and allows the heat to be absorbed by a measured weight of water. By measuring the change in temperature of the water, the number of calories absorbed can be calculated.<sup>1</sup>

*Densities (at room temperature)*

TABLE 1-1

substance	density, g/ml	substance	density, g/ml
hydrogen (gas)	0.00009	table salt	2.16
carbon dioxide (gas)	0.00198	sand	2.32
balsa wood	0.16	aluminum	2.70
cork wood	0.21	iron	7.9
oak wood	0.71	silver	10.5
water	1.00	lead	11.3
eucalyptus wood	1.06	mercury	13.6
magnesium	1.74	gold	19.3

The amount of heat energy required to change the temperature of 1 g of a substance by 1°C is called the **specific heat** of the substance:

$$\text{specific heat} = \frac{\text{no. of calories}}{(\text{no. of grams}) (t_1 - t_2)}$$

where  $t_1$  is the higher centigrade temperature,  $t_2$  the lower. The specific heat of water, of course, is

$$1 \frac{\text{cal}}{(1 \text{ g}) (1 \text{ deg C})} = 1 \text{ cal}/(\text{g} \times \text{deg C})$$

The specific heat of water is high as compared with most substances. A number of specific heats are given in Table 1-2.

## EARLY IDEAS ABOUT CHEMICAL REACTIONS

In the period from about 1600 to 1800 in Western Europe, great advances were made in the study of chemical changes, and chemists stated the first laws describing these changes. Although modern research has brought about modification of these early ideas, an understanding of them is fundamental to the study of chemistry.

## CLASSES OF MATTER

Single pure substances were early classified as either elements or compounds. **Elements** were described as substances that could not

<sup>1</sup> If one knows the number of calories associated with a change, he can calculate the energy in other units if he wishes. For example, 1 cal is equivalent to 41,840,000 or  $4.184 \times 10^7$  ergs. The erg is a minute unit of energy used to express kinetic energy,  $\text{KE} = \frac{1}{2}mv^2$ . If the mass is expressed in grams and the velocity in centimeters per second, the unit of energy is called the erg. The kinetic energy of a mass of 1 g moving at a speed of 1 cm/sec is  $\frac{1}{2}$  erg:

$$\text{KE} = \frac{1}{2} (1 \text{ g}) \left( \frac{1 \text{ cm}}{1 \text{ sec}} \right)^2 = \frac{1}{2} \text{ g} \frac{\text{cm}^2}{\text{sec}^2} = \frac{1}{2} \text{ erg}$$

**CHEMICAL CONCEPTS; SCIENTIFIC  
MEASUREMENTS**

be decomposed by simple chemical change into two or more different substances. Some elements familiar to the early chemist were copper, silver, gold, sulfur, carbon, and phosphorus. **Compounds** were described as substances of definite composition that could be decomposed by simple chemical change into two or more different substances. Common salt is an example of a compound. It can be decomposed into a shiny, active metal (sodium) and a poisonous, greenish-yellow gas (chlorine). The properties of the substances obtained by the decomposition of a compound, of course, are completely unrelated to the properties of the compound. Today, just over 100 elements are known, but there are over 1 million compounds; some familiar compounds are water, sugar, alcohol, carbon dioxide, and ammonia.

**TABLE 1-2**      *Specific heats*

substance	specific heat, cal/(g $\times$ deg C)	substance	specific heat, cal/(g $\times$ deg C)
water	1.000	salt	0.185
alcohol	0.581	carbon	0.127
ice	0.478	iron	0.108
aluminum	0.212	gold	0.0312
sand	0.188	uranium	0.0280

Most materials cannot be classified as single pure substances, because they contain a number of different substances more or less intimately jumbled together. Such materials are called **mixtures**. A mixture has no unique set of properties; rather, it possesses the properties of the substances of which it is composed. Air is an example of a gaseous mixture; it is composed principally of nitrogen, oxygen, argon, water vapor, and carbon dioxide, and each of these substances displays its own unique properties in the mixture. Further, it is usually possible to separate the components of a mixture by physical changes rather than chemical. For example, when the temperature of air is lowered, water vapor tends to separate as liquid or solid water, that is, as dew or frost. On extreme cooling, the carbon dioxide solidifies and then the remainder of the air liquefies. If the liquid air is carefully boiled, the mixture can be separated, because each component tends to boil away at a particular temperature range, depending on its own boiling point. This method of separating the substances in a mixture is called distillation. Figure 1-4 shows a typical simple apparatus that is used in laboratories to carry out distillations of common liquid mixtures that contain components whose boiling points are widely separated.

In describing the appearance of materials, the chemist often finds two terms useful: *homogeneous* refers to material in which no differing parts can be distinguished even with a microscope; *heterogeneous* refers to material in which there are visible differing parts.

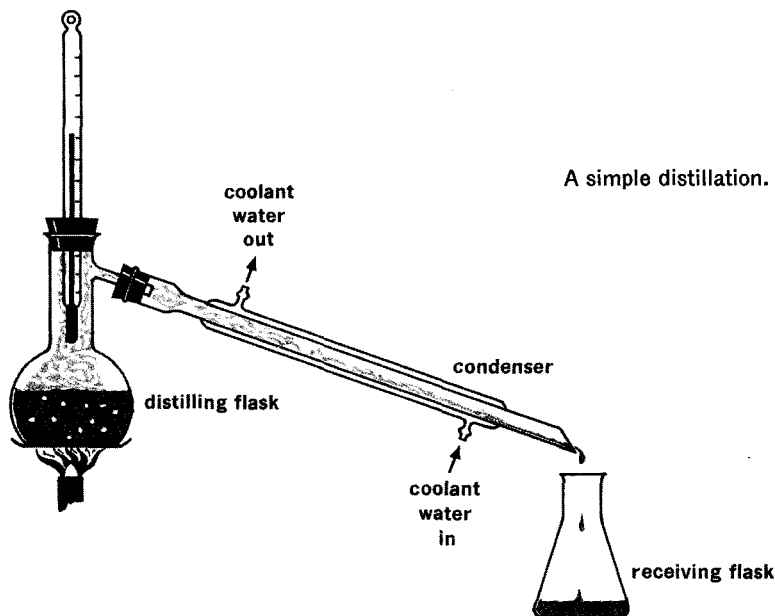


FIG. 1-4

## LAW OF CONSERVATION OF MASS

In the eighteenth century, experimental methods were developed for measuring volumes of gases; weighing gases, liquids, and solids; and conducting chemical reactions in a manner so that the weights of the reactants and the products of a reaction could be precisely measured (Fig. 1-5). Such experiments provided investigators with



burning wood

When wood is burned in open air, matter appears to be destroyed. However, if wood is burned as shown in a closed tube, so that the products of combustion can be collected and weighed, we find that the weights of products, as measured by the gain in weight of the second sodium oxide absorber, is actually more than the weight of the wood burned.

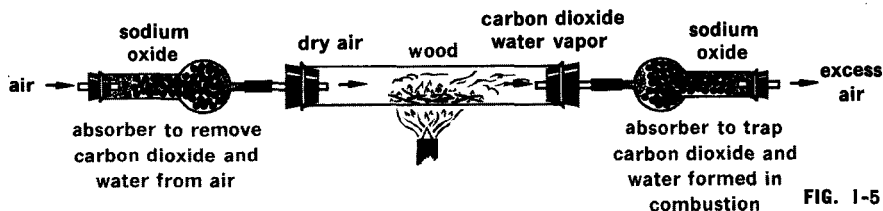
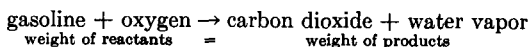


FIG. 1-5

many facts and led to the discovery of a number of fundamental laws describing chemical behavior. According to one of these laws, *mass is neither created nor destroyed in any transformation of matter.*



This statement, which sums up the results of thousands of painstaking experiments, is the **law of conservation of mass**. The facts necessary to support this statement were correlated by M. V. Lomonosov, a Russian, in 1756. Perhaps translation difficulties kept his work from becoming widely known in Western Europe. Antoine Lavoisier, a Frenchman, formulated the law independently in 1783. As an illustration of the law, consider the complete combustion of gasoline. The following relationship is true within the limits of our ability to determine the weights<sup>1</sup> of the reacting substances and the products of the reaction:



## LAW OF DEFINITE COMPOSITION

To determine the composition of a compound, one can decompose a weighed sample of the compound into its constituent elements and determine their individual weights, or one can determine the weight of a compound formed by the chemical union of known weights of the elements. (Other methods are also available; some of them are discussed in Chap. 9.) The study of the composition of many compounds led to the discovery of the following law: *A pure compound is always composed of the same elements combined in a definite proportion by weight.* This is the **law of definite composition** (also called the law of definite proportions).

By way of illustration consider water, whose composition has been determined by experiment many times. The same answer is always obtained. Water as it occurs in nature is composed of hydrogen and oxygen only, and these elements are always in the proportion of 11.19 per cent hydrogen and 88.81 per cent oxygen by weight. Or consider table sugar. The composition of sugar (no matter whether it comes from sugar cane, sugar beet, or maple syrup) as determined by analysis is carbon, 42.1 per cent; hydrogen, 6.5 per cent; oxygen, 51.4 per cent.

## LAW OF MULTIPLE PROPORTIONS

Often, two elements unite to form more than one compound. Analyses show that, although the compounds have different compositions by weight, these compositions are related in a simple way. If a given weight of the first element is considered, say, 1.00 g, it is found that the weights of the second element that will combine with this 1.00 g are related to each other in the ratio of small whole numbers. To take a specific example, let us consider the two common combinations of carbon with oxygen. With good conditions for burning, carbon burns in air to form a dense, nonpoisonous, noncombust-

<sup>1</sup> The interconversion of matter and energy is discussed in Chap. 14.

tible gas; however, if not enough oxygen is present during the burning, a poisonous, combustible gas is also formed. An analysis of these compounds reveals that each gas has its own definite composition. In the noncombustible gas, 1.00 g of carbon is always combined with 2.67 g of oxygen; whereas in the gas that will burn, 1.00 g of carbon is always combined with only 1.33 g of oxygen. We see that the ratio of the weights of oxygen that combine with the same weight of carbon is 2.67:1.33, or 2:1.

Iron and chlorine also form two compounds, ferrous chloride and ferric chloride. The amount of chlorine that combines with 1.00 g of iron in ferrous chloride is 1.26 g; the amount of chlorine combining with 1.00 g of iron in ferric chloride is 1.89 g. The weights of chlorine that combine with the same weight of iron are in the ratio of 1.26:1.89, or 2:3. A formal statement of these facts is known as the **law of multiple proportions**: *When two elements combine to form more than one compound, the different weights of one that combine with a fixed weight of the other are in the ratio of small whole numbers.*

## EARLY ATOMIC THEORY

Simple chemical and physical changes have been studied since the dawn of history. Some of the earliest questions that occurred to the student of nature were: What is matter made of? Is sand made of the same stuff that wood is made of? Is a piece of gold made of tiny pieces of gold, or is it made of tiny pieces of several substances mixed together to make gold?

Questions such as these were pondered by the ancient Greeks, and the rational conclusion that some of them came to was this. If a large piece of gold is cut (*tomos*) in half, both pieces are still gold. If these halves could be divided again and then again and again, one would finally get down to the smallest possible piece of gold. This tiny particle could not be cut (*a-tomos* is Greek for not cut), for it would be the unit particle of gold, a gold atom.

For more than 2,000 years after this early rational beginning, the concept of small particles called atoms influenced man's thinking very little. It was not till the latter part of the seventeenth century that the birth of modern chemistry focused attention on the investigation of material things and led to the recognition of basic differences between elementary and complex substances. Indeed, it was not till early in the nineteenth century, about 1803, that the English chemist John Dalton stated his famous atomic theory of matter. Dalton's atomic theory was based directly on the ideas of elements and compounds and on the three empirical laws of chemical combination just described.

**Dalton's Atomic Theory.** John Dalton was an English school-teacher who developed the first modern theory of *atoms* as the

## CHEMICAL CONCEPTS; SCIENTIFIC MEASUREMENTS

smallest particles of elements and *molecules* as the smallest particles of compounds. To explain the properties of elements, he developed the idea that an element contained only one kind of atom and that an atom was a simple, indestructible particle of matter. Elements, he said, could not be changed to simpler substances, because their atoms could not be broken down.

Dalton explained the constant composition of compounds by the theory that atoms of elements were joined to make more complex particles called molecules, which were the simplest units of compounds. According to Dalton, the favored atomic combination for just two elements was probably 1:1. Because all the molecules were identical, the compound would have a constant composition, having a greater percentage by weight of the element that had the heavier atom. Some of the early diagrams of atoms and molecules are shown in Fig. 1-6.

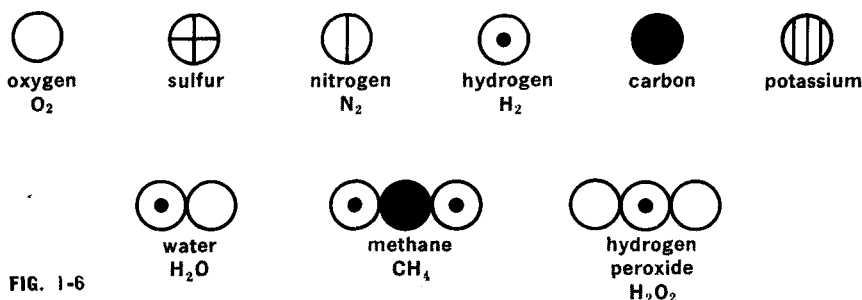


FIG. 1-6

Some of Dalton's symbols for elements and compounds. The correct formulas are given when his were in error.

The law of conservation of mass was easily explained also. The theory held that in any chemical reaction atoms could change their partners in composition, or molecules could be broken down into atoms; but the total number of atoms in the reactants and the products would be the same. If atoms were indeed indestructible, no mass could be gained or lost in a chemical reaction.

The law of multiple proportions is very nicely accounted for if one assumes that under some conditions atoms of two types combine in a 1:1 combination and under other conditions they combine in a 1:2 or 1:3 or 2:3 or some other combination. If we go back to the example that we considered earlier of the two oxides of carbon, we will recall that the ratio of amounts of oxygen that combined with a given amount of carbon under two different conditions was 2:1. With diagrams like Dalton's we can clearly show how the weight of oxygen per weight of carbon could be twice as great in one case as in the other, if we assume a 1:1 atomic combination in one case and a 1:2 in the other, as shown schematically in Fig. 1-7. In modern symbols a molecule of the first oxide is given the formula CO and is named

Dalton postulated that in one oxide of carbon one atom of oxygen is combined with one atom of carbon, and that in the other oxide two atoms of oxygen are combined with one atom of carbon.



FIG. 1-7

carbon monoxide. The formula for a molecule of the second is CO<sub>2</sub> and is named carbon dioxide.

Dalton's atomic theory can be summarized by listing the following assumptions:

1. All matter is made up of tiny, indestructible unit particles called atoms.
2. The atoms of a given element are all alike.
3. During chemical reactions atoms may combine, or combinations of atoms may break down; but the atoms themselves are unchanged.
4. When atoms form molecules, they unite in small whole-numbered ratios, such as 1:1, 1:2, 1:3, 2:3.

Although some of these assumptions have been shown to be incorrect by later work, Dalton's theory was a guiding principle for a century of brilliant chemical discoveries.

**Relative Atomic Weights.** Dalton's atomic theory, coupled with the determination of the composition of many compounds, led to the development of a scale of relative weights of atoms. Consider the example of carbon monoxide. We saw earlier that, to form this compound, 1.00 g of carbon combined with 1.33 g of oxygen. If we assume that the carbon monoxide is a collection of billions upon billions of molecules all with the formula CO, it is clear that each oxygen atom must be one-third heavier than each carbon atom. If we could determine the weight of the oxygen atom, the weight of the carbon atom could be calculated.

Although Dalton thought water should have the formula HO, later workers showed that H<sub>2</sub>O explained the known facts better. In the case of water, 1 g hydrogen combines with 8 g oxygen. If we assume that the compound is a collection of billions upon billions of molecules all with the formula H<sub>2</sub>O, it is clear that each oxygen atom must be sixteen times heavier than each hydrogen atom.

It was not possible for Dalton and his contemporaries to determine the weight of a single atom or even to show for sure that atoms existed at all. But they could assume that atoms had definite weights and assign relative atomic weights to them that agreed with the known compositions of compounds.

A few years after Dalton's initial work, oxygen atoms were arbitrarily assigned the relative weight of 16. The weights of other atoms were compared with oxygen by analyzing as many compounds as possible and working out the most likely formulas for these compounds. In the case of the three elements that we have mentioned, the relative weights of H:C:O are 1:12:16.

## CHEMICAL CONCEPTS; SCIENTIFIC MEASUREMENTS

In Chap. 16, we say more about an early chemical method of determining relative atomic weights. The chemical method, however, is hardly used at all today, because of the discovery of a more precise, modern method that we describe in the next chapter.

## CHAPTER REVIEW

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*The Chapter Reviews are divided into two sections. In the first section the principal terms or topics introduced in the chapter are listed, and you will find it helpful to practice writing discussions of each of these. Every student needs a good desk-size dictionary because it provides a great deal of chemical information, including definitions of many technical terms.*

*The second section in the Chapter Review includes both numerical and verbal exercises which require application of principles discussed in the chapter. For problems, your attention is called to the sections in the Appendix on arithmetical procedures, uses of units, and significant figures.*

*The answers to many of the problems are given in the Appendix. However, they should be used to check your work only after you have obtained the solution.*

### Terms

Rationalism, empiricism, reproducible, law, hypothesis, theory, intrinsic and extrinsic properties, physical and chemical properties, chemical and physical changes, chemical reaction; energy—kinetic, heat, potential, radiant, chemical, atomic, and nuclear; exothermic, endothermic, law of conservation of energy, scientific measurements, metric system units, factor-unit method, exponent, mass, weight, density, calorie, centigrade scale, Celsius scale, specific heat, element, compound, mixture, homogeneous, heterogeneous, law of conservation of mass, law of definite composition, law of multiple proportions, early Greek atomic theory, Dalton's atomic theory, molecule, relative atomic weight.

### Exercises

- Convert each of the following numbers to the exponential form (see Appendix):
  - 381,000,000
  - 0.00001
  - 0.000763
  - $\sqrt{0.000001}$
  - $\frac{1}{10,000}$
- Perform the indicated calculations, first converting individual numbers to powers of 10 if they are not expressed that way:
  - $12,000 \times 6.0 \times 10^{-4}$
  - $0.00001 \div 0.0000002$
  - $2.5 \times 10^3 \times 4.0 \times 10^{-4}$
  - $\sqrt{3 \times 10^2 \times 12 \times 10^6}$

e.  $\frac{1}{0.0005} \times \frac{1}{0.000002}$

f.  $1 + 10 + 0.1$

3. a. 3.0000 gal of liquid X weighs 20.0 lb. What does 1 gal weigh? (See Appendix on significant figures.)  
 b. 3.0000 gal of X weighs  $2.000 \times 10^1$  lb. What does 1 gal weigh?  
 c. 3.0000 gal of X weighs  $2.0 \times 10^1$  lb. What does 1 gal weigh?
4. What is the number of significant figures in each of the following numbers: 325; 3.25;  $3.25 \times 10^6$ ;  $3.2500 \times 10^6$ ; 1 gal?
5. Make the following conversions, following the factor-units method (see Appendix for a description of this method and for conversion factors):  
 a. 5 cm to millimeters  
 b. 200 cm to meters  
 c. 300 ml to liters  
 d. 300 ml to quarts  
 e. 5 in. to centimeters  
 f. 10 oz to grams  
 g. 100 mg to kilograms
6. The diameter of a gold atom is 3 Å. What is its diameter in inches?
7. a. The volume of a quantity of liquid was determined as 10.08 ml. What is the volume in cubic centimeters?  
 b. The volume of the liquid above was determined more precisely as 10.07832 ml. What is the volume in cubic centimeters?
8. An object has a mass of 10.1 g. If one could take this object to the moon and there redetermine its mass, what would he find it to be? (The gravitational attraction on the moon is about one-sixth of that on earth.)
9. a. On a cold day, the temperature may drop to  $-10^\circ\text{F}$ . What is the temperature on the centigrade scale?  
 b. The temperature of the hottest part of the flame of a Bunsen or Tirrill burner is about  $800^\circ\text{C}$ . What is this temperature in degrees Fahrenheit?  
 c. At what temperature are the readings on Fahrenheit and centigrade thermometers the same?
10. Calculate the amount of heat needed to change the temperature of 1 gal of water from:  
 a. 20 to  $30^\circ\text{C}$   
 b. 70 to  $212^\circ\text{F}$
11. What is the weight in pounds of a cube of iron measuring 1.0 ft on an edge?
12. A piece of metal weighing 20.12 g was immersed in a quantity of water in a graduated cylinder. The initial volume of the water was 15.5 ml; the volume of the metal and water was 21.5 ml. Calculate the density of the metal.



## CHEMICAL CONCEPTS; SCIENTIFIC MEASUREMENTS

13. A length of aluminum wire weighs 1 lb. What is the weight of an equal length of the same diameter iron wire; of a gold wire?
14. Thirty-two grams of oxygen contains  $6.02 \times 10^{23}$  oxygen molecules. Calculate the weight of one molecule (a) in grams and (b) in pounds.
15. The longest and shortest wavelengths of light that can be detected visually are about 7,000 Å (red) and 4,000 Å (blue), respectively. Convert these wavelengths to centimeters.
16. Common table salt is a free-flowing, granular, water-soluble, white solid that has no tendency to lose its flavor on standing in dry air. Which of the foregoing are extrinsic and which are intrinsic properties? Which are physical properties; chemical properties?
17. A solution contains 10 g of salt per liter of solution. What weight of salt is present in 50 ml of solution?
18. What volume of air is required to burn 5 gal of gasoline? Densities of air and gasoline are 1.3 g/liter and 690 g/liter, respectively; 110 g of gasoline requires 2,500 g of air for its combustion.
19. A piece of aluminum weighing 10.0 g and at a temperature of 90.0°C is placed in 100 g of water at a temperature of 20.0°C. Assuming that no heat is lost to the surroundings, what is the resulting temperature of the aluminum and water?
20. A cylindrical rod weighing 50.0 g is 20.0 cm long and 2.00 cm in diameter. Calculate the density.
21. Two different compounds of elements A and B were found to have the following composition: first compound, 1.188 g of A combined with 0.711 g of B; second compound, 0.396 g of A combined with 0.474 g of B.
  - a. Show that these data are in accord with the law of multiple proportions.
  - b. If the formula for the first compound is  $AB_2$ , what is the formula for the second?
22. Explain how Dalton's atomic theory gives a satisfactory explanation of why no measurable amount of matter is destroyed when wood burns.

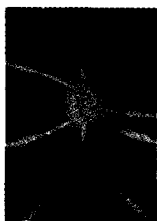
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# ATOMIC STRUCTURE;

## THE PERIODIC TABLE



### EARLY CLASSIFICATION OF ELEMENTS

The concept of an atom as a simple, indestructible particle was generally accepted by scientists during the nineteenth century. One reason for this acceptance was that no methods were available for studying particles as small as atoms. In this chapter we first trace the development of an early scheme of classifying elements, and we then take up some of the marvelous discoveries of the present century which revealed details of atomic structure and which provided a basis for our modern scheme of classifying elements.

**Symbols.** The medieval alchemists used symbols to stand for elements, such as a crescent  $\smile$  for silver, symbolic of the silvery color of the moon, or a circle  $\bigcirc$  for gold, symbolic of the golden sun and of perfection. Dalton made up other symbols, as suggested by Fig. 1-6. Our present system of using letters as symbols was begun by a contemporary of Dalton's, the Swedish chemist J. J. Berzelius (1779-1848). He began by using the first letter of the name of the element as a symbol. Examples include those which we used in Chap. 1: H is the symbol for hydrogen, O for oxygen, and C for carbon. Because the names of several elements begin with the same letter, Berzelius found it convenient to use two letters in some symbols. Thus, carbon, calcium, chlorine, and cobalt are designated by the symbols C, Ca, Cl, and Co, respectively. Note that the first letter of the symbol is capitalized, the second is not. In some cases, the symbols we use today are related to the Latin names common centuries ago. For example, the symbols for silver (Ag), copper (Cu),

and iron (Fe) are derived from the Latin names *argentum*, *cuprum*, and *ferrum*, respectively. The symbols for the known elements are listed with their names inside the back cover.

## PERIODIC BEHAVIOR OF ELEMENTS

One of the first attempts at grouping similar elements was made from 1817 to 1830 by Johann Döbereiner, when he grouped similar elements in threes, or *triads*. He noted that iron, cobalt, and nickel were alike in many ways, as were also chlorine, bromine, and iodine.

Between 1864 and 1869 a number of men, including John Newlands in England, Lothar Meyer in Germany, and Dmitri Mendeleev in Russia, came to realize that an exciting unifying principle applied to the elements that they knew. These early chemists found that, if they listed the elements in the order of increasing atomic weight, elements with similar properties appeared at fairly regular intervals in the list. Properties such as melting points, boiling points, and chemical activities were found to vary in a roughly periodic way, rising, falling, rising again, falling again as the atomic weight increased.

The plot of boiling points versus atomic weights in Fig. 2-1 shows a roughly periodic variation. Modern data are used in this plot; also, a number of elements not known to the chemists of a century ago are included. It is of interest to find that the colorless, gaseous elements He, Ne, Ar, Kr, and Xe not only have very low boiling points but are the least active chemically of the elements. Because of their resistance to chemical reaction they are called the *noble gas family*. Another group of similar elements, each of which follows one of the noble gases, is Li, Na, K, Rb, and Cs. Not only do these elements have similar boiling points, but each is a soft, malleable metal; and as a group they are the most active chemically of all the metals. Observations such as these indicate that the periodic variation of physical and chemical properties is an extremely important characteristic of the elements.

**Mendeleev's Periodic Table.** Dmitri Mendeleev was the first person to arrange the elements clearly and concisely according to their periodic similarities. In his first periodic table he listed the elements in order of increasing atomic weight unless this order conflicted with his desire to group similar elements. As we shall see later in this chapter, the *atomic number*, a feature unknown to Mendeleev, is a more fundamental guide in correlating properties than is atomic weight. In modern periodic tables the elements are listed strictly in order of increasing atomic number. Among the naturally occurring elements, there are four instances in which an increase in atomic number is not accompanied by an increase in atomic weight: for numbers 18 and 19, 27 and 28, 52 and 53, and 90 and 91. A modern

Nb  $\uparrow$  Mo

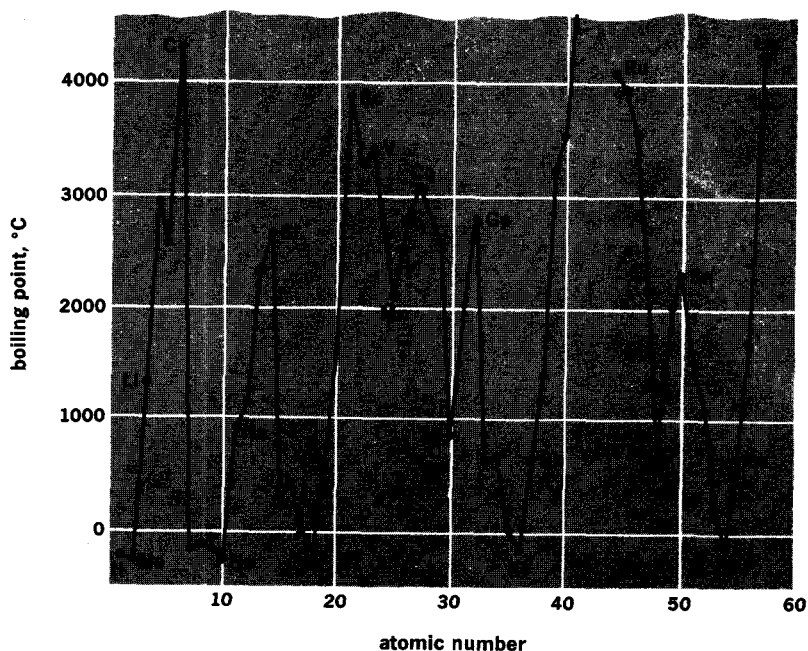


FIG. 2-1

As the atomic numbers increase, the boiling points of the elements vary in a roughly periodic way. Several elements are identified by symbols on the graph; others may be identified by checking their atomic numbers and symbols in Fig. 2-2. The boiling points of niobium and molybdenum are so high that they are off the graph.

statement of the periodic law is: *The physical and chemical characteristics of the elements are periodic functions of their atomic numbers.*

Figure 2-2 shows a modern periodic table that is arranged on a basis similar to that used in Mendeleev's original table. Above the symbol for each element is its atomic number, and below the symbol is the atomic weight as precisely determined by modern methods.

In 1869 the atomic numbers were unknown, and some of the elements had not been discovered. It was part of Mendeleev's outstanding contribution to chemistry that he recognized a more fundamental way of arranging the elements than a rigid adherence to a regular increase in atomic weight. His arrangement was based largely on periodic physical similarities such as melting points, boiling points, and densities, and on such periodic chemical similarities as the tendencies to combine with other elements and the types of compounds formed. Knowing that there were groups of similar elements, Mendeleev arranged most of the known elements in a table so that similar elements appeared in the same vertical column. This and other features of periodic tables will be taken up in detail at the end of this chapter, where we discuss one of the modern arrangements.

		RH	RH <sub>2</sub>		RH <sub>3</sub>		RH <sub>4</sub>		RH <sub>3</sub>		RH <sub>2</sub>		RH					
type of oxide		R <sub>2</sub> O	RO		R <sub>2</sub> O <sub>3</sub>		RO <sub>2</sub>		R <sub>2</sub> O <sub>5</sub>		RO <sub>3</sub>		R <sub>2</sub> O <sub>7</sub>		RO <sub>4</sub> (except noble gases)			
period	group	group	group	group	group	group	group	group	group	group	group	group	group	group				
	I	II	III	IV	V	VI	VII							VIII				
1	1																	
	H																	
	1.0080																	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B		B	B	
	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓		↓	↓	
2	3	4	5	6	7	8	9											
	Li	Be	B	C	N	O	F											
	6.939	9.012	10.81	12.011	14.007	15.999	18.998											
3	11	12	13	14	15	16	17											
	Na	Mg	Al	Si	P	S	Cl											
	22.99	24.31	26.98	28.09	30.974	32.06	35.453											
4	19	20	21		22	23	24	25	26	27	28	29	30					
	K	Ca			Ti	V	Cr	Mn	Fe	Co	Ni							
	39.102	40.08			47.90	50.94	52.00	54.94	55.85	58.93	58.71							
	39	40	41		42	43	44	45	46	47	48	49	50					
	Cu	Zn			As	Se	Br											
	63.54	65.37			74.92	78.96	79.904											
5	37	38	39	40	41	42	43		44	45	46	47	48	49	50	51	52	
	Rb	Sr	Y	Zr	Nb	Mo			Ru	Rh	Pd							
	85.47	87.62	88.90	91.22	92.91	95.94			101.07	102.90	106.42							
	47	48	49	50	51	52	53		54	55	56	57	58	59	60	61	62	
	Ag	Cd	In	Sn	Sb	Te	I											
	107.87	112.40	114.82	118.69	121.75	127.60	126.90											
6	55	56	57	58		59	60	61	62	63	64	65	66	67	68	69	70	
	Cs	Ba	*La			Ta	W			Os	Ir	Pt						
	132.90	137.34	138.91			180.93	183.85			190.23	192.22	195.08						
	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	
	Au	Hg	Tl	Pb	Bi													
	196.97	200.59	204.37	207.19	208.98													
7																		

\*lanthanide series

58						65					
Ce						Tb					
140.12						158.93					

†actinide series

90		92									
Th		U									
232.04		238.03									

FIG. 2-2

A modern periodic table based on Mendeleev's original arrangement. Elements in the darker boxes were not known in 1869. See the comment about element 102 on page 375. Element 104 has been reported by scientists in the U.S.S.R., as pointed out in Chap. 14.

It has been said that the discovery of the periodic behavior of the elements was the most important milestone in the history of chemistry. Certainly it has stimulated and guided a great deal of work. Mendeleev foretold the existence of unknown elements, because there were some blank spots in his table. In about 1871 he predicted that an element like aluminum, one like boron, and one like silicon would some day be found. These bold predictions spurred other scientists to search for new elements; as a result, gallium, Ga (similar to aluminum), was found in 1875; scandium, Sc (similar to boron), in 1879; and germanium, Ge (similar to silicon), in 1886.

The existence of the noble gases was not predicted on the basis of the periodic table. However, when these six elements were discovered between 1894 and 1900, they were found to fit nicely into the periodic arrangement, each one terminating a row in the periodic table. Also, the elements following uranium—Mendeleev's table ended with this element—that have been synthesized in recent years by nuclear bombardment fall in period 7. The table does not predict an upper limit for the number of elements that can be made by nuclear bombardment, but it seems now that not many more elements will be produced this way because of the great instability of such atoms (see Chap. 14).

## CHANGING IDEAS ABOUT ATOMS

John Dalton wrote his papers on atomic theory in the first decade of the nineteenth century. For almost 100 years his ideas were influential in stimulating and guiding the experimental work of chemists throughout the world. Toward the end of that century, Dalton's atoms were accepted almost as real by many persons, because the idea of tiny particles had been used so successfully in interpreting chemical discoveries of all sorts. The concept of atoms as the fundamental particles of elements, with each element having its invariable atomic weight, was an idea that Mendeleev and others accepted. However, the periodic classification of the elements indicated that there might be features of atomic structure then unknown that could account for the periodic changes in properties of elements.

In a few years just at the end of the last century, the easily understood world of the indestructible atom was completely overturned by a series of astounding discoveries—X rays in 1895, radioactivity in 1896, the electron in 1897, and radium in 1898. During these years laboratory tools and techniques were developed that laid the groundwork for half a century of investigation of the subatomic world, the work of microphysics. The new ideas of atomic structure that grew out of this research are the bases for our modern understanding of chemical phenomena. One of the most influential of these new ideas concerns electrons, small charged particles which are contained in all atoms and whose arrangements in atoms help explain

why the properties of elements are periodic and why there are families of similar elements.

Another important idea stemmed from the observations of radioactivity. Atoms of some elements were indeed not indestructible but broke apart spontaneously, throwing off small charged particles and thereby changing into atoms of other elements.

## EXPERIMENTAL EVIDENCE FOR EXISTENCE OF VERY SMALL PARTICLES

*Nature of Charged Bodies.* Since earliest recorded history men have known about the effect of rubbing two dissimilar objects together; each of the objects, if handled carefully, has a strange effect on certain other things that it touches. A comb rubbed against dry hair attracts strands of the hair or even picks up pieces of tissue paper; if two balls of pith are touched with a glass rod that has been rubbed with a silk cloth, they repel each other; if a plastic rod is rubbed with paper, the plastic causes the "leaves" of an electroscope to repel one another.

When two dissimilar objects are rubbed together briskly, (1) one of the objects takes on a positive charge, the other a negative charge; (2) an object with one charge attracts an object with a charge of opposite sign; (3) two objects having charges of the same sign repel each other.

Suppose a piece of plastic and a piece of paper are rubbed together until they become charged. If they are then placed in contact and held together for a short time, they will become neutral again; that is, their total charges will redistribute equally.

But the paper and the plastic need not touch directly. If the two charged bodies are kept far apart but are connected by a piece of metal wire, both of them become neutral again. This shows that the charge can travel along a wire. The passage of a charge along a wire is called a *current of electricity*.

The behavior of charged particles as they travel through air or a vacuum has been studied by many persons who wished to learn something of the nature of tiny fragments of matter far too small to be seen even with the most powerful microscopes. Figure 2-3 shows the movement of two charged particles, positive (+), and negative (-), caused by the presence of charged wires or plates called **electrodes**. The positively charged electrode is the **anode**, the negatively charged one the **cathode**. The greater the charges on the anode and the cathode, the greater the attraction they have for oppositely charged particles.

An interesting adaptation of the electrodes is shown in Fig. 2-4. A hole is cut in the anode, and the charges on the electrodes are made very intense. The cathode is made rather small in order to concentrate the effect of its charge over a small area. Negative

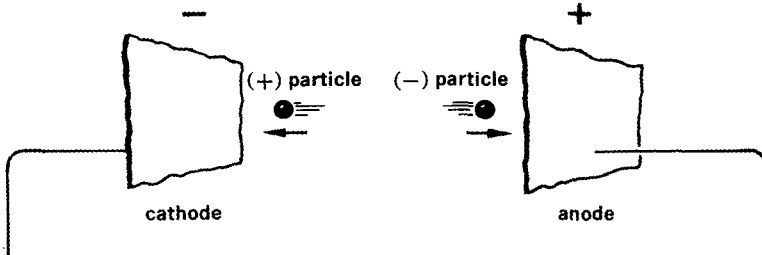


FIG. 2-3

A charged particle is attracted to an electrode of opposite charge and repelled by an electrode of the same charge.

particles, repelled by the large charge on the cathode and attracted by the large charge on the anode, may move toward the anode with such great velocities that some fail to hit the plate and go through the hole instead. Many of the negative particles strike the anode, but the few that happen to speed through the hole continue on as a *beam of particles*. If we wish to produce a narrow beam of particles whose direction is precisely known, we can place a metal plate with a small hole or slit in the path of the beam. Only the particles that are traveling in a narrow straight path pass through the second hole.

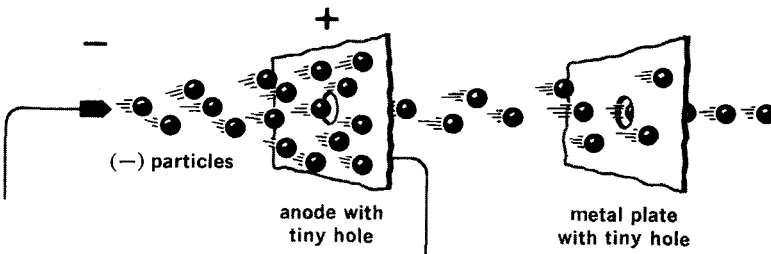


FIG. 2-4

A few of the charged particles speeding toward an electrode with a hole in it may by chance speed through the hole instead of striking the electrode.

The direction of travel of charged particles can be influenced by bringing electrically charged plates (electrostatic forces) or magnets (magnetic forces) close to their paths. If the charged plates are not too highly charged, the speeding particles are not drawn to the plates but are only deflected from their original paths (see Fig. 2-5). In the case of a magnet, the charged particles are not attracted to either pole of the magnet; preferably their path of travel is in a plane that is at right angles to the magnetic field (see Fig. 2-6), with positive particles being forced in one direction, negative particles in the opposite direction.

The *velocities* of particles, their *charges* and *masses*, and the *magnitudes* of the *electrical* and *magnetic forces* required to deflect the



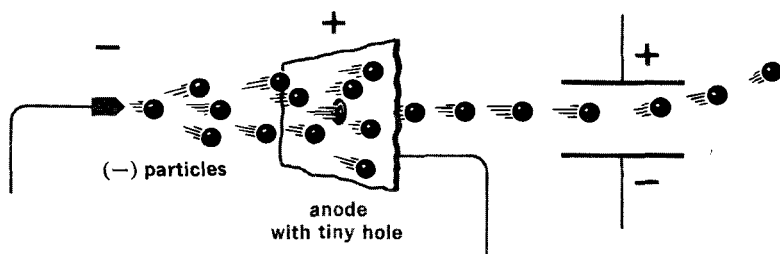
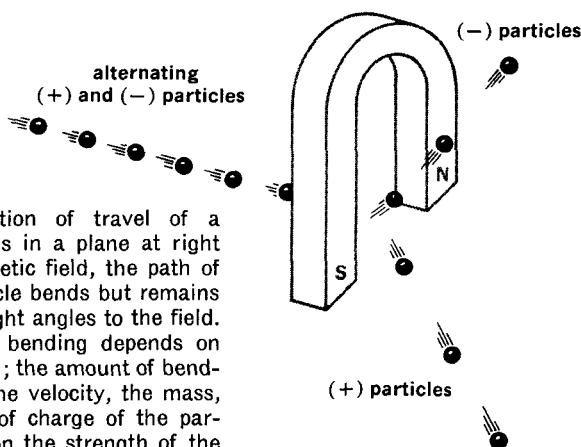


FIG. 2-5

Charged particles travel in a straight line unless acted on by an outside force. Passing near charged plates, they are deflected from a straight path.



When the direction of travel of a charged particle is in a plane at right angles to a magnetic field, the path of the charged particle bends but remains in the plane at right angles to the field. The direction of bending depends on the type of charge; the amount of bending depends on the velocity, the mass, and the amount of charge of the particle, as well as on the strength of the magnetic field.

FIG. 2-6

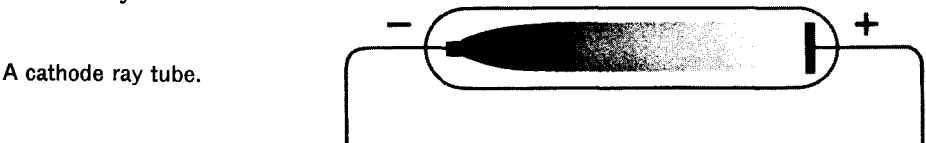
particles by certain amounts—all these quantities are interrelated by well-established physical laws. Knowing the direction in which particles moving in an electrical or magnetic field are deflected and the amount of deflection under carefully controlled conditions, physicists can calculate the charges and masses of particles that are too small to be seen directly.

Finally, we should note two experimental techniques of great practical importance. First, most of the experiments with tiny moving charged particles are carried out in evacuated containers of glass or metal, because particles of air interfere with the free movement of tiny particles. Second, because the moving particles are too small to be seen, special methods are required to follow their motion. These methods depend on the effects that the particles have when they collide with certain substances. Some substances emit visible light (fluoresce) when struck by fast-moving particles (see Fig. 2-8). Another simple detector is photographic film, which is affected by tiny fast-moving particles in much the same way as it is by being exposed to light. If we put a piece of film in the path of a beam of

particles, we can detect the areas in which a number of particles strike the film. The developed film will be darkened in the spots struck by particles; the area and degree of darkening are related to the number of bombarding particles.

## EXPERIMENTAL EVIDENCE FOR THE ELECTRON

If two wires are subjected to a high electrical potential and then brought close together, a spark or arc jumps from one wire to the other. If the ends of the two wires are sealed in a glass tube (as shown in Fig. 2-7) that is then highly evacuated, the discharge from one wire to the other is more gentle. The greenish glow or luminescence that is emitted from the negative wire, or cathode, is caused by the cathode ray.<sup>1</sup>



A cathode ray tube.

FIG. 2-7

First studied intensively in 1858 by J. Plücker, cathode rays have been shown to have the following properties:

1. They travel in straight lines away from the cathode.
2. They are negatively charged. This is evident from the fact that they are attracted by a positively charged plate. Also, the rays' path is bent by a magnetic field in the same way as the path of particles known to be negative (Fig. 2-8).

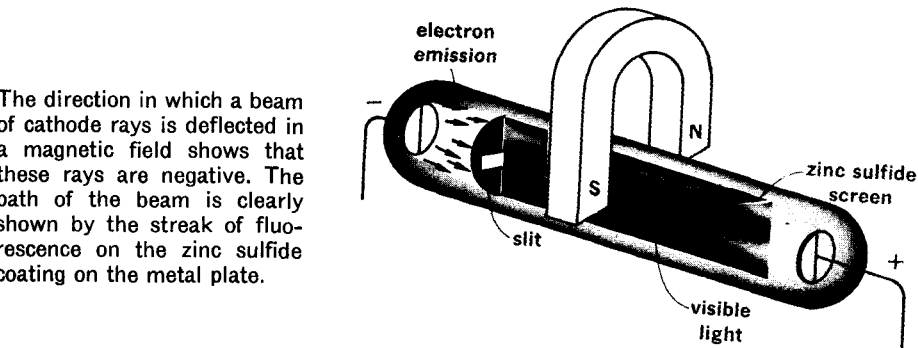


FIG. 2-8

<sup>1</sup> When cathode rays (high-speed electrons) strike matter, they may give rise to certain effects: glass emits a faint yellowish-green glow; zinc sulfide emits a green glow. If the vacuum tube contains a little neon gas, the molecules of the gas emit a red glow; helium gas molecules emit a pink glow. One of the most important effects of cathode rays, discovered in 1895 by W. C. Roentgen, is that material that is struck by high-velocity electrons may emit a penetrating radiation called **X rays**. X rays have no mass and no charge; they are true electromagnetic radiation, similar to light waves or radio waves, but of higher frequency than either. (See Table 3-1.)

3. The cathode rays consist of particles with definite mass. From the speed of the particles (about one-tenth that of light), their charge, and their deflection in a magnetic field of known strength, the mass of individual particles has been calculated as  $1/1,838$  that of the lightest known atom, the hydrogen atom. These particles are called electrons.

4. The nature of the cathode rays (electrons) is the same irrespective of (a) the material of which the cathode is made, (b) the type of residual gas present in the evacuated tube, (c) the kind of metal wires used to conduct the current to the cathode, and (d) the materials used to produce the current.

All this evidence, especially the last item, indicates that electrons are fundamental particles found in all matter. No charge smaller than that on one electron has ever been found. For convenience, this charge has been assigned a value of  $1-$ .

### NUCLEUS OF THE ATOM

*Rutherford's Experiment.* One type of particle emitted by radioactive materials is the alpha particle, a unit that has a mass about four times that of a hydrogen atom and a charge opposite in sign and twice the magnitude of the charge of the electron, that is,  $2+$ . Because they have velocities of about 10,000 miles/sec, alpha particles can be thought of as tiny high-speed projectiles.

In 1908–1909 H. Geiger and E. Marsden, working under the great English physicist Ernest Rutherford, reported some of the most meaningful experiments of modern times. By a fluorescent method, they were able to show that alpha particles of low penetrating power could go right through a thin sheet of solid gold. However, the most important facts that they observed were that a few of the

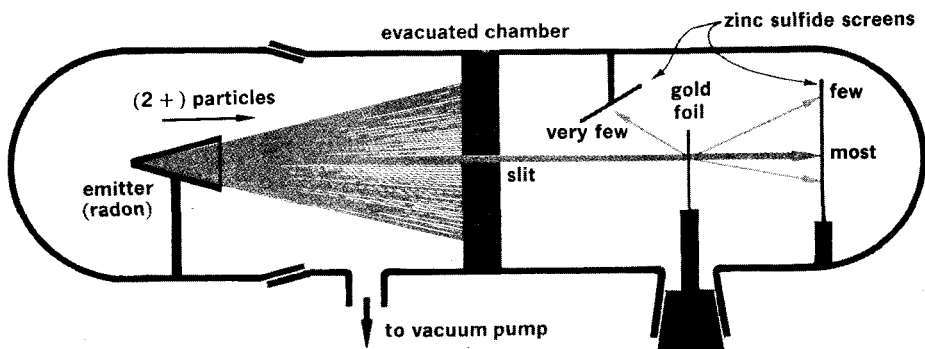


FIG. 2-9

A schematic representation of several experiments in which gold foil was bombarded with a beam of alpha particles. Zinc sulfide emits a flash of light when struck by an alpha particle.

Rutherford's interpretation of the bombardment of gold atoms with alpha particles. The tiny dots on the left represent alpha particles; the spheres represent gold atoms; the tiny dot in the center of each sphere is the nucleus of the atom. (In any drawing of this size it is necessary to greatly exaggerate the sizes of the alpha particles and the nuclei relative to the sizes of the atoms.)

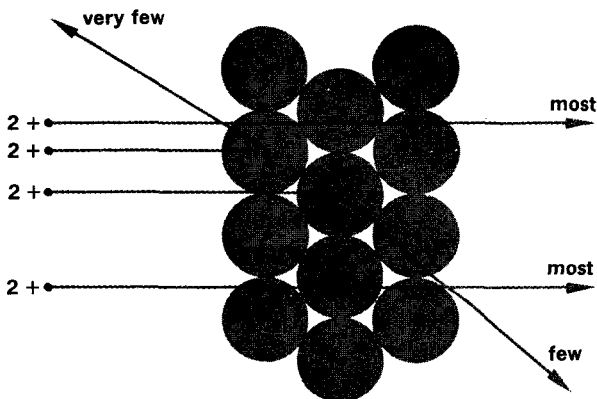


FIG. 2-10

alpha particles were deflected from their straight path and that some of these even bounced back from the gold foil. As Rutherford remarked later, "It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you."

Gold was chosen as the target because it is a very malleable metal that can be beaten into extremely thin sheets, possibly only 100 atoms thick. Like other solids, however, gold can hardly be compressed at all, so one assumes that its atoms are packed tightly together. As shown in Fig. 2-9, the experimenters observed three things, principally: most of the alpha particles went straight through the supposedly closely packed gold atoms; a small percentage of the particles was apparently deflected by something; and a very few of the alphas were bounced back from the gold.

Even for the fertile mind of a genius, it takes time to correlate new facts and to frame theories to explain them. According to Geiger, Rutherford walked into the laboratory on a day in 1911, saying, "I've got it." What he had was a clear mental picture of a relationship between the bombarding alpha particles and the gold atoms. He had worked out an explanation of all the observed facts in terms of a new concept of atomic structure. He pictured a model similar to that which is shown in Fig. 2-10. The nucleus of each atom is a tiny, massive, positive unit. The nucleus is so small that only rarely does an alpha particle chance to pass near. The nucleus evidently repels alphas, so the nucleus must be positive. The fact that an alpha occasionally bounces back shows that the nucleus of a gold atom must be considerably heavier than the bombarding alpha particle. The outer electrons are far away from the nucleus; they form the outside surface of the atom. Between the nucleus and the outer electrons is empty space except for other electrons.

Our present information, gleaned largely from X-ray investigations, indicates that the diameter of an atom is about  $10^{-8}$  cm. It has

## ATOMIC STRUCTURE; THE PERIODIC TABLE

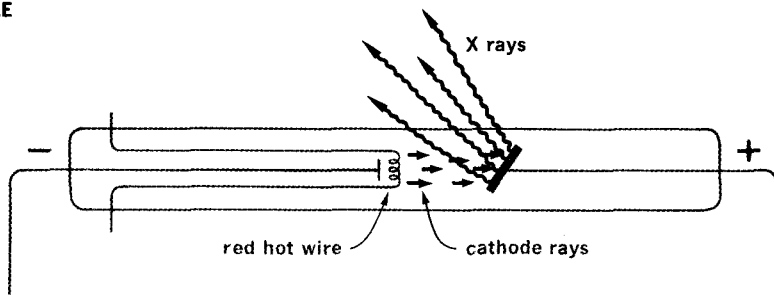
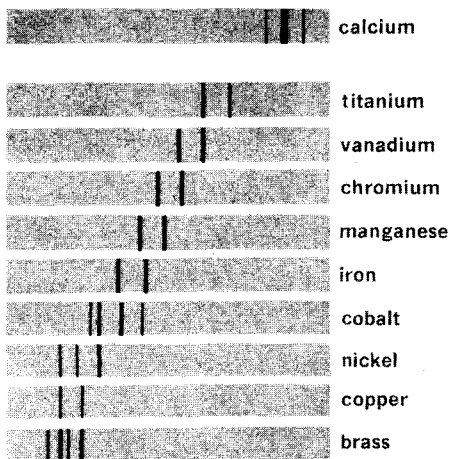


FIG. 2-11

Diagram of an X-ray tube.

been estimated that a nucleus has a diameter of about  $10^{-13}$  cm, or only 1/100,000 that of the atom.

**Atomic Number.** At the same time that Rutherford was developing his concept of the nuclear atom, one of his coworkers, H. G. J. Moseley, discovered that different elements emitted *characteristic X rays* when used as the anodes in an X-ray tube (Fig. 2-11). When Moseley tabulated his X-ray results, he found that the wavelengths of the X rays emitted decreased regularly as the atomic weights of the elements increased. After studying his data, Moseley was able



An artist's copy of some of Moseley's historic X-ray photographs. The X rays emitted by different elements were diffracted by a crystalline substance toward photographic plates. The positions of the lines on the plates are directly related to the wavelengths of the X rays. Of these elements, calcium emits the longest wavelength (least energetic), and zinc (which is mixed with copper to make brass) emits the shortest wavelength (most energetic).

FIG. 2-12

to state that the number of positive charges on the nucleus "increases from atom to atom by a single electronic unit. . . ." This number of positive charges is now called the **atomic number** and is 1 for hydrogen, 2 for helium, 3 for lithium, etc. We can define an element in terms of modern atomic theory: An element is a substance all of whose atoms have the same atomic number.

Figure 2-12 is an artist's conception of photographic records collected by Moseley. Note how the wavelengths of the X rays decrease

in stepwise fashion from calcium to zinc (brass, an alloy of copper and zinc, shows lines characteristic of both these elements). The more energetic the X ray emitted, that is, the shorter its wavelength, the greater is the positive charge on the nucleus of the atom. Moseley calculated the charge on the nucleus of a calcium atom to be  $20+$ ; of a titanium atom,  $22+$ ; vanadium,  $23+$ ; and so on to zinc,  $30+$ .

Of great importance is the fact that Moseley's determination of atomic numbers agreed with Mendeleev's periodic arrangement. It further justified Mendeleev's decision to rely on properties even when the order of increase in atomic weights was misleading. For example, after Moseley's discovery, the atomic numbers of tellurium and iodine were found to be 52 and 53, respectively; this is consistent with Mendeleev's placement of Te before I.

**Proton.** Even before the electron was identified, E. Goldstein, in 1886, noticed that a fluorescence appeared on the inner surface of a cathode-ray tube behind a cathode perforated with holes. This finding indicated that positive rays were moving in such a tube, some of which sped through the holes in the cathode and struck the end of the tube.

After the discovery of the electron, physicists devoted a great deal of effort to seeking a fundamental particle with a positive charge. Studies of cathode-ray tubes indicated that many different types of positive particles could exist, depending on the gas used to flush out the tube prior to evacuation. In the course of these studies a positive particle was found which had a *charge* equal in size but opposite in sign to that of the electron and which had a *mass* almost equal to that of a hydrogen atom. This subatomic positive particle, the **proton**, is formed in cathode-ray tubes that contain a little hydrogen gas. It is assumed that the high-speed electrons knock electrons off the neutral hydrogen atoms, leaving the positive nuclei behind. These positive particles travel in a direction opposite to that of the negative cathode rays and can be shown to be particles of unit positive charge with a mass equal to  $1,837/1,838$  that of the hydrogen atom.

The fact that the proton was found to be about 1,837 times as heavy as the electron supported Rutherford's theory of the nuclear atom very well. The light electrons could, at relatively great distances, surround a nucleus that might be made of the heavy, positive protons collected together. Additional support for this theory was afforded by Moseley's findings. The heavier the atom, the greater the positive charge on the nucleus. The evidence indicated that an atom of hydrogen had 1 proton in its nucleus, a helium atom had 2, a lithium atom 3, and so on. The atomic number, then, is the number of protons in the nucleus. It follows from the modern definition of an element that the atoms of an element are alike in that their nuclei contain the same number of protons.

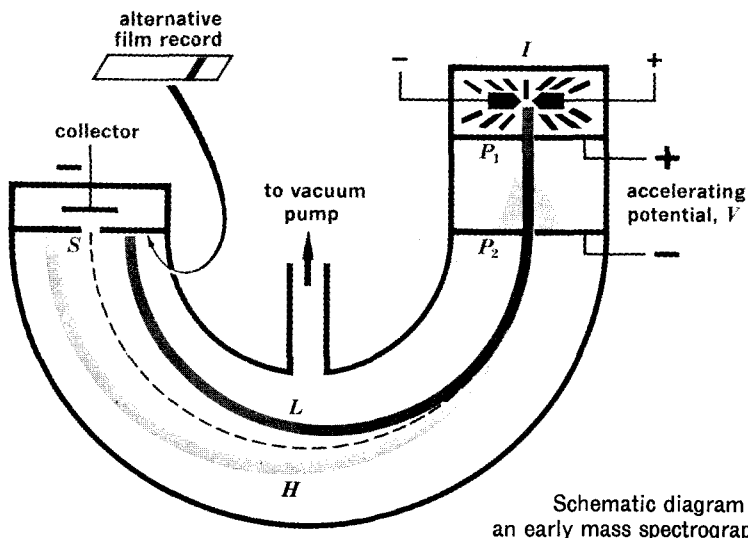


FIG. 2-13

Schematic diagram of  
an early mass spectrograph.

In order to determine if atoms could be thought of as being made solely of protons and electrons, it was necessary to determine the weights of specific atoms and to compare these weights with the total weights of the protons and electrons thought to be involved per atom.

**Mass Spectrograph.** Seeking to compare the weights of atomic-sized particles directly, J. J. Thomson and F. W. Aston, just prior to World War I, experimented with the deflection of streams of charged gaseous particles by means of known magnetic and electrostatic forces. After the war, Aston in England and other workers around the world perfected an apparatus called the mass spectrograph with which they compared the weights of atoms precisely.

A schematic diagram of one of the early mass spectrographs developed by A. J. Dempster, of Chicago, is shown in Fig. 2-13. Atoms of an element are bombarded by cathode rays at *I* so that electrons are knocked off the atoms, forming positively charged particles called *ions*. (An atom that loses electrons becomes a positively charged ion; one that gains electrons becomes a negative ion.) The positive ions formed at *I* are accelerated by a high voltage (800 to 1,000 volts) in the area between the charged plates *P*<sub>1</sub> and *P*<sub>2</sub>. A stream of ions speeds at high velocity through the slit in *P*<sub>2</sub> into the semicircular space *A*. Space *A* is between the poles of a powerful magnet. The magnet imposes a field of sufficient strength to cause the stream of ions to follow curved paths. If the ions are of different masses, the paths of the heavier ions *H* are not curved so much as those of the lighter ones *L*. Professor Dempster found that by varying the accel-

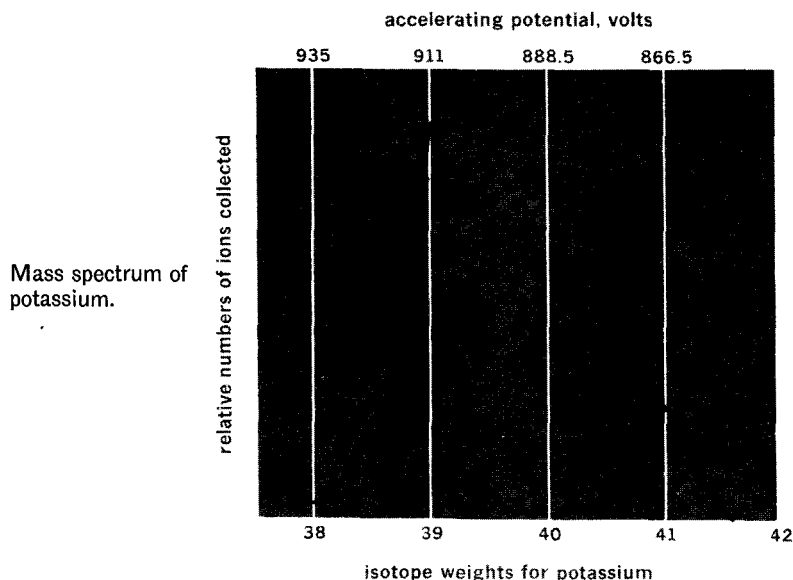


FIG. 2-14

erating voltage between plates  $P_1$  and  $P_2$  he could cause either heavy or light ions to go through a slit  $S$  and be measured by a negatively charged collector. Since the masses of the different ions that go through slit  $S$  are inversely proportional to the original accelerating voltage,<sup>1</sup> the masses of different ions can be compared. With the element potassium, Dempster found the results that are shown in Fig. 2-14. He knew from other measurements that most potassium atoms had an atomic weight of 39. Ions of these atoms were focused in his mass spectrograph when  $V$  was 911 volts. At the lower voltage of 866.5 volts other potassium ions were focused on slit  $S$ . The weights of the other ions were then calculated as 39 times 911/866.5, or 41. As indicated in Fig. 2-14, the lighter potassium ions (39) are more abundant than the heavier ones (41).

<sup>1</sup> For a charged particle accelerated by a potential field, the mass  $m$ , velocity  $v$ , charge  $e$ , and voltage of field  $V$  are related as follows:

$$\frac{1}{2} mv^2 = eV$$

For a moving particle in a magnetic field of strength  $H$ , the radius of curvature  $r$  is related to  $m$ ,  $v$ , and  $e$  as follows:

$$\frac{mv^2}{r} = Hev$$

By combining these equations, we find

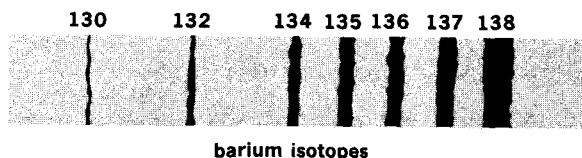
$$m = \frac{eH^2r^2}{2V}$$

In Dempster's mass spectrograph  $r$  is the curvature that brings the particles to slit  $S$  (Fig. 2-13),  $H$  is held constant, and  $e$  is the unit electronic charge on an ion. Because all factors are constant except  $m$  and  $V$ ,  $m$  is inversely proportional to the accelerating voltage  $V$ , which is carefully varied and measured.



Atoms of the same element that have different weights are called **isotopes**. The first isotopes discovered were those of neon by Thomson and Aston in 1912-1913. Since that time isotopes for practically all the elements have been discovered. The mass spectrograph has been developed into a very precise instrument that can determine atomic masses to 1 part in 10,000. Some instruments record results in photographic form, as shown in Fig. 2-15.

Precise mass spectrographic measurements provide the best means of determining atomic weights of elements. The standard for atomic weights has recently (1961) been established as the most common isotope of carbon. The weight of this isotope is arbitrarily defined as exactly 12 atomic weight units, and all other atoms are compared with it.<sup>1</sup> One **atomic weight unit (awu)** is defined as one-twelfth the weight of one carbon-12 atom.



Artist's copy of a mass spectrum recorded photographically. (A. J. Dempster, *Phys. Rev.*, 49: 947 [1936].)

barium isotopes

FIG. 2-15

In the case of potassium (Fig. 2-14), precise measurements show that 93.1 per cent of the atoms weigh 38.98 awu and 6.9 per cent weigh 40.97 awu. There is a third, very rare isotope (39.98) with an abundance of 0.01 per cent. Neglecting the rare isotope, we can calculate the approximate average atomic weight of potassium:

$$\text{average atomic weight} = (0.069)(40.97) + (0.931)(38.98) = 39.1$$

For a more precise calculation we would need to take all three isotopes into account, and we would use the most precise values of atomic weight units available. This type of calculation shows the average atomic weight of potassium to be 39.102 awu.

In Table 2-1 the weights of the isotopes and the average atomic weights of several common elements are listed.

**Neutron.** By means of the mass spectrograph it has been determined that the proton has a weight of 1.0073 awu; the weight of the electron is 0.00055 awu. We see from Table 2-1 that the mass of the lighter hydrogen isotope can be accounted for by picturing a nucleus of 1 proton and 1 electron outside the nucleus. But none of the other cases is so simple. Consider the isotopes of nitrogen. This element has an atomic number of 7, which indicates that nitrogen

<sup>1</sup> Prior to 1961, the standard for chemical atomic weights was natural oxygen, which was given the weight of 16. The adoption of carbon-12 as a standard changed all atomic weights by 43 parts in 1 million: (old atomic weight) = (1.000043) (new atomic weight). Carbon-12 was chosen to replace oxygen because it is more convenient to use in the mass spectrograph.

*Isotopic weights and average atomic weights*

TABLE 2-1

element	mass number (nonradioactive isotopes)	isotopic weight, awu	isotopic abundance, per cent	average atomic weight, awu
hydrogen	1	1.0078	99.98	1.008
	2	2.0141	0.02	
carbon	12	12.0000	98.9	12.011
	13	13.0033	1.1	
nitrogen	14	14.0031	99.62	14.007
	15	15.0001	0.38	
oxygen	16	15.9949	99.76	15.9994
	17	16.9991	0.04	
	18	17.9992	0.20	
sulfur	32	31.972	95.06	32.064
	33	32.971	0.74	
	34	33.968	4.18	
	36	35.967	0.02	
chlorine	35	34.969	75.4	35.453
	37	36.966	24.6	

atoms contain 7 protons and 7 electrons. But such atoms would weigh only a little more than 7 awu, whereas nitrogen atoms weigh about 14 and 15 awu, respectively. All known atoms, except the lighter hydrogen isotope described in Table 2-1, have weights that are much greater than the sum of the weights of their protons and electrons.

The fact that the weight of the protons and electrons does not account for the total masses of atoms led scientists to search for an uncharged particle whose presence would explain the additional weight of an atom but not upset the balance of charges between protons and electrons. Because it had no charge, this elusive particle escaped detection for years. But in 1932 neutrons were identified by J. Chadwick.<sup>1</sup> A **neutron** has no charge and has a mass of 1.0087 awu, that is, about the same as that of a proton.

With the discovery of the neutron, chemists were able to account for the main features of atoms in terms of three fundamental particles (see Table 2-2). An atom is defined as an extremely small, electrically neutral particle that has a tiny but massive positive core or nucleus and one or more electrons relatively far outside its nucleus. The number of protons plus neutrons in the nucleus is the **mass number** of the atom.<sup>2</sup> It follows that the mass number minus the number of

<sup>1</sup> The experimental details of the identification of the neutron are presented in Chap. 14.

<sup>2</sup> The alert student will find that the weight of a particular isotope of an element is not precisely equal to the sum of the weights of the protons, neutrons, and electrons that it contains. A detailed discussion of this interesting point is delayed till Chap. 14.

**TABLE 2-2**      *Fundamental particles of matter*

\* The charge of an electron is defined as the elementary unit of charge. Its absolute value is  $4.80298 \times 10^{-10}$  electrostatic unit (esu).

$$\begin{array}{rcc} \text{mass number} & - & \text{atomic number} = \text{number of neutrons} \\ 36 & & 16 \qquad \qquad 20 \end{array}$$

Just how big are particles of atomic dimensions? No atom has ever been seen, even through the most powerful optical microscopes. Physicists have been able, however, to measure the volume occupied by a known number of atoms and thus calculate the volume of the individual particle. If the atom is assumed to be spherical, its diameter can be calculated. Table 2-3 lists a number of common measure-

**TABLE 2-3**      *Measurements*

distance to farthest observed galaxy	$5.0 \times 10^9$ light-years	$4.5 \times 10^{27}$ cm
distance to nearest star	4.3 light-years	$4 \times 10^{18}$ cm
diameter of earth	8,000 miles	$1.3 \times 10^9$ cm
height of average man	68 in.	$1.7 \times 10^2$ cm
diameter of a penny	0.75 in.	1.9 cm
diameter of red blood cell	$3 \times 10^{-4}$ in.	$7.6 \times 10^{-4}$ cm
diameter of smallest virus	$4 \times 10^{-7}$ in.	$1 \times 10^{-6}$ cm
diameter of uranium atom	$1 \times 10^{-8}$ in.	$2.5 \times 10^{-8}$ cm
diameter of hydrogen atom (smallest atom)	$4 \times 10^{-9}$ in.	$1 \times 10^{-8}$ cm
diameter of electron	$1.1 \times 10^{-13}$ in.	$2.8 \times 10^{-13}$ cm
diameter of proton	$4.7 \times 10^{-14}$ in.	$1.2 \times 10^{-13}$ cm

ments of large and small objects. From the value of  $2.5 \times 10^{-8}$  cm given for the diameter of the uranium atom, we can calculate that it would take a line of  $7.6 \times 10^7$ , or 76 million, uranium atoms placed side by side to span the diameter of a penny, a distance of 1.9 cm. Man's successes in measuring the vastness of the universe and the minuteness of the atom stand as two of his great experimental achievements.

Tiny fractions of centimeters are as inconvenient for expressing lengths of atomic size as are tiny fractions of grams for expressing weights. A common unit for describing the sizes of atoms is the **angstrom** (A), defined in Table 1 of the Appendix. Atoms range in size from the hydrogen atom, with a diameter of about 1 A, to the cesium atom, with a diameter of about 5 A.

## ARRANGEMENTS OF ELECTRONS IN ATOMS

The Rutherford concept of the massive, tiny, positive nucleus of an atom surrounded by negative electrons led to a most perplexing question. How are the electrons, which contribute hardly any mass, arranged so that they take up practically all the space occupied by an atom? This problem was attacked by many physicists. The fundamental breakthrough to understanding is usually credited to Niels Bohr, whose studies of atomic spectra we discuss in Chap. 3, but work done by James Franck and Gustav Hertz to test Bohr's ideas provided another kind of evidence for the arrangement of electrons.

Franck and Hertz measured the energy, in electron volts, of cathode rays required to knock electrons off atoms and form ions. One electron volt (ev) is the energy acquired by a singly charged particle when it falls through a potential of one volt.<sup>1</sup>

**Ionization Energies of Atoms.** Suppose that a sample of a gaseous element is collected at very low pressure in a cathode-ray tube. The energy of the cathode ray, measured in electron volts, required to knock the most loosely bound electron off a gaseous atom is called the first ionization energy of the element:



For atoms with enough electrons, a second electron can be knocked off at a higher potential, a third at a still higher potential, and so on.

In Table 2-4 some of the ionization energies of the first 22 elements, expressed in electron volts, are listed. Careful study of these data has helped the physicist form his ideas about the arrangement of the electrons outside the atomic nucleus. For example:

1. Potassium, K, sodium, Na, and lithium, Li, atoms have low

<sup>1</sup> The electron volt is a much smaller unit of energy than the erg. One electron volt =  $1.602 \times 10^{-12}$  erg.

ATOMIC STRUCTURE; THE  
PERIODIC TABLE

TABLE 2-4 *Ionization energies, ev*

atomic number	symbol	1st $e^-$	2nd $e^-$	3rd $e^-$	4th $e^-$	5th $e^-$
1	H	13.595				
2	He	24.580	54.40			
3	Li	5.390	75.6193	122.420		
4	Be	9.320	18.206	153.850	217.657	
5	B	8.296	25.149	37.920	259.298	340.127
6	C	11.264	24.376	47.864	64.476	391.986
7	N	14.54	29.605	47.426	77.450	97.863
8	O	13.614	35.146	54.934	77.394	113.873
9	F	17.42	34.98	62.646	87.23	114.214
10	Ne	21.559	41.07	64	97.16	126.4
11	Na	5.138	47.29	71.65	98.88	138.60
12	Mg	7.644	15.03	80.12	109.29	141.23
13	Al	5.984	18.823	28.44	119.96	153.77
14	Si	8.149	16.34	33.46	45.13	166.73
15	P	11.0	19.65	30.156	51.354	65.007
16	S	10.357	23.4	35.0	47.29	72.5
17	Cl	13.01	23.80	39.90	53.5	67.80
18	Ar	15.755	27.62	40.90	59.79	75.0
19	K	4.339	31.81	46	60.90	
20	Ca	6.111	11.87	51.21	67	84.39
21	Sc	6.56	12.89	24.75	73.9	92
22	Ti	6.83	13.63	28.14	43.24	99.8

SOURCE: Reprinted by permission from Therald Moeller, *Inorganic Chemistry*, John Wiley & Sons, Inc., New York, 1952.

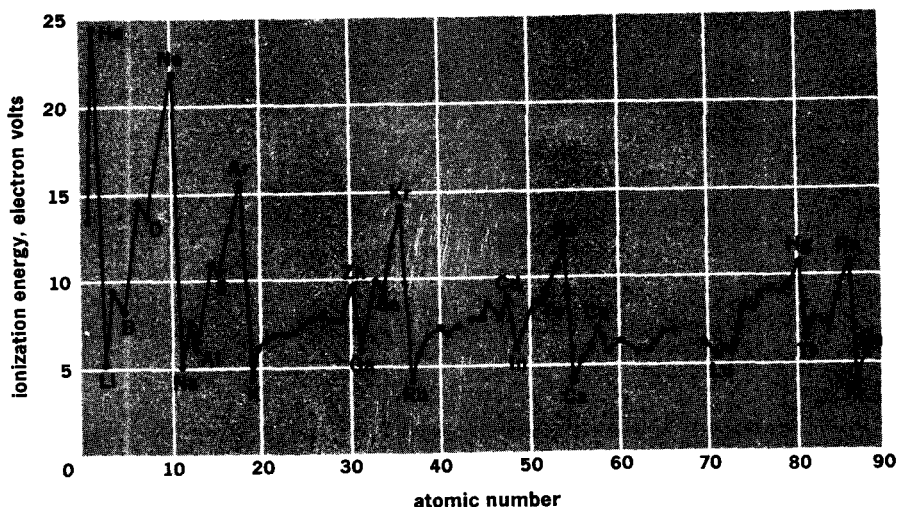
first ionization energies; this indicates that each has 1 electron that is knocked off easily. That the second ionization energy for these atoms is much higher indicates that their other electrons are more strongly held.

These facts indicate that potassium, sodium, and lithium atoms each have 1 electron that is far from the positive nucleus and is loosely held. This outer electron is in a high energy level; the other electrons are in one or more energy levels nearer the nucleus.

2. Magnesium, Mg, and calcium, Ca, have low first and second ionization energies; this indicates that each has 2 electrons that are knocked off easily. Note that these elements have two of the lowest second ionization energies listed.

These data indicate that magnesium and calcium atoms each have 2 electrons that are far from the positive nucleus and are loosely held. Their remaining electrons are in energy levels nearer the nucleus and are more tightly held.

3. Helium, He, neon, Ne, and argon, Ar, atoms have very large first ionization energies. This means that these atoms hold on to all their electrons very tightly. (These so-called noble gases are found to be chemically quite inactive; that is, they hardly ever interact with other substances in chemical reactions.)



First ionization energies plotted against atomic numbers.

FIG. 2-16

From the total number of electrons in these noble-gas atoms it has been calculated that helium has a single energy level containing 2 electrons and that neon and argon each have 8 electrons in their outside energy levels.

When the first ionization energies are plotted against atomic numbers, as in Fig. 2-16, the energy required to knock an electron off an atom is seen to vary in a periodic way as the atomic numbers increase. Note that the noble gases are at the top of each of the periodic peaks of the curve.

**Main Energy-level Divisions.** On the basis of the study of atomic spectra, ionization energies, and the periodic table, physicists have come to think of the electrons in unexcited atoms as being arranged in one to seven major energy levels, depending on the complexity of the atom. The first energy level, which can hold only 2 electrons, is thought to be closest to the nucleus, because these electrons are held very strongly. In the energy levels at greater distances from the nucleus, the number of electrons that each level can hold increases, and their attraction for the nucleus decreases.

## MODERN FORM OF THE PERIODIC TABLE

With the discovery of the arrangements of electrons in atoms chemists achieved a satisfying explanation of Mendeleev's periodic table. Usually, elements in the same family have atoms with the same number of electrons in their outer energy levels, although

ATOMIC STRUCTURE; THE  
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IA		IIA		IIIA		IVA	
hydrogen	H·						
 $1e^-$		beryllium	Be:	boron	B:	carbon	C:
 $2e^- 1e^-$		 $2e^- 2e^-$		 $2e^- 3e^-$		 $2e^- 4e^-$	
sodium	Na·	magnesium	Mg:	aluminum	Al:	silicon	Si:
 $2e^- 8e^- 1e^-$		 $2e^- 8e^- 2e^-$		 $2e^- 8e^- 3e^-$		 $2e^- 8e^- 4e^-$	
potassium	K·	calcium	Ca:				
 $2e^- 8e^- 8e^- 1e^-$		 $2e^- 8e^- 8e^- 2e^-$					

FIG. 2-17

there are a number of exceptions in B families. Evidently the number of electrons in the outer energy level is the most important factor in determining the chemical and physical characteristics of an atom. Also the work of Moseley, in showing how to determine the atomic numbers of elements, provided a better guide than atomic weights for listing the elements in order. The modern statement of the **periodic law** is: *The physical and chemical characteristics of the elements are periodic functions of their atomic numbers.* The periodic variation of the number of electrons in the outer shells of atoms of the first 20 elements is shown in Fig. 2-17.

A popular form of the periodic table today is the *long form*, a copy of which appears inside the front cover. The major divisions of this form of the periodic table are much the same as those in the Mendeleev table, but the long form brings out the periodic relationships between properties and atomic number a little more clearly.

Because we shall use the table inside the front cover continually, it is to our advantage to be thoroughly familiar with it. There are sixteen vertical divisions into groups or families, because the A and B families of the eight groups are listed separately. There are seven horizontal rows or periods, and each of the first six periods ends with a noble gas.

For each element there are (1) the symbol, (2) the atomic number (in gray), (3) the atomic weight, and (4) the number of electrons in each of the principal energy levels of the atom. There are six complete periods; the seventh is incomplete. The first has only two members; the other complete ones have 8, 18, or 32 members. There are eight groups, numbered I to VIII. In each group the A family always includes two elements from periods 2 and 3, whereas the B family has none from these short periods. The following families illustrate these points:

				VIII A	
VA		VIA		VIIA	
nitrogen $\cdot\dot{\text{N}}\cdot$ $2e^- 5e^-$		oxygen $\cdot\ddot{\text{O}}\cdot$ $2e^- 6e^-$		fluorine $\cdot\ddot{\text{F}}\cdot$ $2e^- 7e^-$	helium $2e^-$ He:
phosphorus $\cdot\dot{\text{P}}\cdot$ $2e^- 8e^- 5e^-$		sulfur $\cdot\ddot{\text{S}}\cdot$ $2e^- 8e^- 6e^-$		chlorine $\cdot\ddot{\text{Cl}}\cdot$ $2e^- 8e^- 7e^-$	neon $2e^- 8e^-$ :Ne:
					argon $2e^- 8e^- 8e^-$ :Ar:

Schematic representation of atoms of the first 20 elements, showing the periodic variation of electrons in the outer energy levels. In the abbreviated version, using dots around symbol, each dot represents an electron in the outermost energy level.

IIA family: Be, Mg, Ca, Sr, Ba, Ra

IIB family: Zn, Cd, Hg

VIIA family: F, Cl, Br, I, At

VIIB family: Mn, Tc, Re

The table is arranged so that similar elements are in the same family. For example, family IB, the copper family, is made up of the metals copper, Cu, silver, Ag, and gold, Au. An element is usually more like a member of its own family than it is like any element in another family.

The elements in the A family of a group are not usually physically similar to the elements in the B family of the same group. In most areas of the table the A and B families of a group are also chemically dissimilar. For example, the A family of group II is made up of very active metals (Mg, Ca, etc.), whereas the B family is made up of considerably less active metals (Zn, Cd, Hg).

*Usefulness of the Periodic Table.* In subsequent chapters, as we study the chemical and physical behavior of many of the elements, we shall find that ability to interpret the periodic table is an important help. First, the periodic table is an aid to memorizing and understanding chemical data. A glance at the symbols in group IA helps us remember that there are a number of elements that in some ways resemble the well-known metal sodium, Na. These elements are lithium, Li, potassium, K, rubidium, Rb, cesium, Cs, and probably francium, Fr, although the last one is so rare that it has not been studied a great deal.

Second, the table is a guide to chemical prediction and theory, because it enables us to determine which elements should be similar



to one another. Not only do similar elements act alike, but their compounds may also be alike. For example, NaCl, sodium chloride or common table salt, has some properties that are similar to those of both KCl and RbCl, because sodium, Na, potassium, K, and rubidium, Rb, have some common characteristics.

Once a student has gained confidence in using the table, not only is he able to reason from a common compound, such as sulfuric acid, whose formula is  $\text{H}_2\text{SO}_4$ , and write the formula of a rarer one,  $\text{H}_2\text{TeO}_4$ , but he may successfully predict some of the ways in which the latter will differ from  $\text{H}_2\text{SO}_4$ .

## CHAPTER REVIEW

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### *Terms*

Chemical symbol, periodicity of properties, noble gases, triads, periodic table, electron, electrode, current of electricity, cathode, anode, beam of particles, electrostatic force, magnetic force, fluoresce, cathode ray, atomic nucleus, alpha particle, Rutherford's metal-foil experiment, atomic number, element, proton, mass spectrograph, atomic weight unit, neutron, isotope, angstrom, electron arrangements, ionization energy, electron volt, main energy levels, periodic law, applications of periodic table.

### *Exercises*

1. Write the symbols for all the elements that you could probably find in and about your home. You should be able to list 15 or more. (They need not be pure; compounds do not count.)
2. What is meant by the statement, "The average daily temperature is a periodic function of time"? Do you consider the relationship a precise one? Explain.
3. After Mendeleev devised his periodic table, he concluded that the atomic weights of certain elements had been incorrectly determined, and this was found to be true to a limited extent. How was Mendeleev able to predict that certain atomic weights were in error? Why was his prediction not valid in all cases?
4. Why are the gases in group VIIIA called noble gases?
5. In 1871, Mendeleev predicted that the element that we now call gallium would some day be discovered. How was he able to do this?
6. Can the periodicity of the properties of elements be explained in terms of Dalton's atomic theory? How (if answer is Yes); why (if answer is No)?
7. How could one show that there are two kinds of charged particles?
8. Since alpha and beta particles cannot be seen, even with a microscope, how are they detected?

9. Suppose that you have built two cathode-ray tubes in such a way that no substance used in making the first tube is used in the second. Suppose also that the electricity used to operate these tubes is generated in different ways so there is no duplication of materials used. You find that the beta rays emitted in the two tubes are identical. What explanation can you advance to account for this observation? Would you be inclined to call your explanation a theory or a hypothesis? Why?
10. What did Rutherford assume to be true of atoms to allow for the passage of most of the alpha particles through the metal foil? How did he account for the occasional deflections?
11. Calculate the kinetic energy in ergs of an alpha particle if its velocity is 10,000 miles/sec. (An alpha particle has a mass of 4 awu.)
12. What experimental observations led Rutherford to conclude that the nucleus of an atom contains most of the mass of the atom?
13. How do X rays resemble ordinary light? How do they differ?
14. When platinum is the target anode of an X-ray tube, X rays of a shorter wavelength are emitted than when the target anode is nickel. How does modern atomic theory account for this?
15. Criticize the statement: An element is a substance made up of atoms all of which are alike.
16. In determining the masses of atoms with a mass spectroscope, the atoms have to be first converted into ions. Why? How?
17. The average weight of sulfur atoms is 32.06 awu. Calculate this weight in grams and in pounds.
18. The natural isotopes of iron have masses of 53.94, 55.93, 56.94, and 57.93. The relative abundances in the same order are 5.82, 91.66, 2.19, and 0.33 per cent. Calculate the atomic weight of iron.
19. The first ionization energy of chlorine is larger than that of sodium. How can we account for this in terms of modern atomic theory?
20. Does an alpha particle have sufficient energy to knock an electron off a sodium atom, thus producing the  $\text{Na}^+$  ion? Show calculations. (See Exercise 11.)
21. The first ionization energy of sodium is larger than that of potassium. How can we explain this fact in terms of atomic theory?
22. The first, second, and third ionization energies of magnesium are 7.644, 15.03, and 80.12 ev, respectively. What do these data indicate about the structure of magnesium atoms?
23. Why should more energy be required to knock off the second electron of an atom than required for the first?
24. Name the element that is in group I, is a member of a B family, and is in period 6.
25. Although the neutron was not discovered till 1932, its existence was suspected several years prior to this. Discuss two separate sets of facts that indicated its existence.

**ATOMIC STRUCTURE; THE  
PERIODIC TABLE**

26. Do the first ionization energies vary in a regular way as the atomic number increases? Is the variation through the second period comparable with that in the third period; with that in the fourth period? Explain.
27. Calculate the velocity of an alpha particle having just enough kinetic energy to produce the  $\text{He}^+$  ion by collision with a helium atom. (See Exercise 11.)
28. If the gold foil with which Rutherford worked was 1/10,000 in. thick, what is a probable minimum number of gold atoms that an alpha particle passed through before hitting the fluorescent screen? The radius of a gold atom is 1.5 Å.
29. Discuss the contribution of each of the following toward the development of a systematic classification of the elements: Johann Döbereiner, John Newlands, Lothar Meyer, Dmitri Mendeleev.

**SUPPLEMENTARY READING**

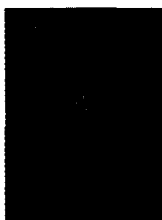
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# ELECTRONIC

## STRUCTURE OF

### ATOMS

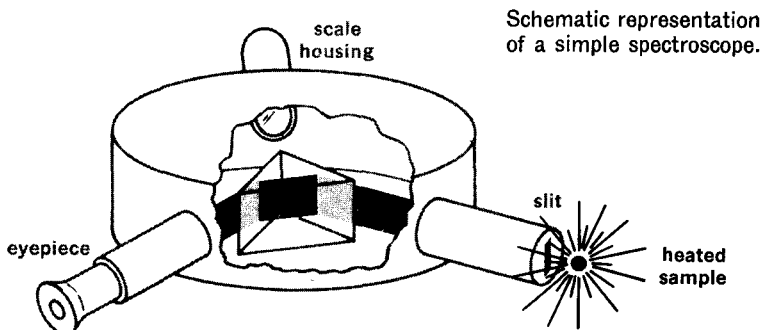


As mentioned in the preceding chapter, a most important early discovery relating to the arrangement of electrons was made by Niels Bohr in 1913. At that time the puzzle of electron arrangement was being intensively investigated by many persons. One of the properties of elements that had been studied carefully for many years, since the invention of the spectroscope in 1859, was the radiation emitted by excited elements. It fell to Bohr to use the fascinating patterns revealed by the spectroscope to unlock the mystery of electronic structure, an achievement for which he received the Nobel Prize in 1922.

### ATOMIC SPECTRA

**Emission Spectra.** When an element absorbs sufficient energy, for example, from a flame or an electric arc, it emits radiant energy. The radiation emitted may fall within the range of visible light, but not necessarily so. When this radiation is passed through a prism in a spectroscope, it is separated into component wavelengths to form an image called an emission spectrum. Emission spectra are of two types: *continuous* and *discontinuous*. For the latter, the image (spectrum) consists of a characteristic pattern of bright lines on a dark field.

**FLAME SPECTRA.** Although any element can be heated to incandescence, some elements have only to be heated in a bunsen flame to make them emit a characteristic colored light. Such elements include lithium, sodium, potassium, calcium, and strontium. A convenient method of testing a substance for the presence of these elements is to dissolve a bit of the material in water and then dip a loop of platinum wire into the solution. If a droplet of the solution is care-



**FIG. 3-1**

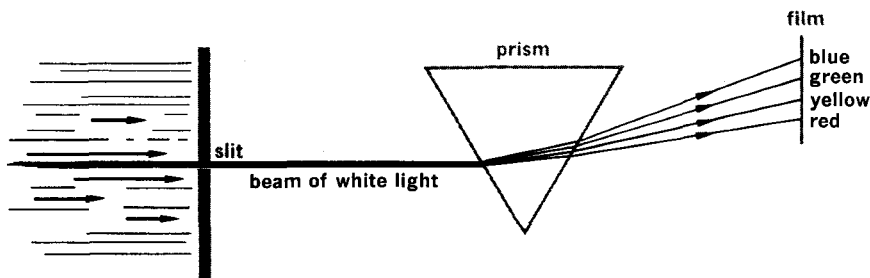
fully evaporated on the wire and then heated in the hot flame of a laboratory burner, the flame has a color characteristic of the elements present.

An element can often be identified by visual observation of the flame and reference to a list such as this one:

element	flame color	element	flame color
lithium	red	cesium	blue
sodium	yellow	calcium	orange-red
potassium	violet	strontium	brick red
rubidium	red	barium	green

For truly positive identification visual observation is insufficient; for example, many persons would have difficulty in distinguishing between a lithium and a strontium flame.

**SPECTROSCOPES.** Precise analysis of the color of a flame can be made with a relatively simple prism spectroscope, such as the one shown schematically in Fig. 3-1. The heart of the instrument is a glass prism that bends the path of any light going through it and bends the paths of different colors to different degrees, as diagramed in Fig. 3-2. By looking at a flame through the eyepiece and rotating



**FIG. 3-2**

The separation of different wavelengths by a glass prism. See also Fig. 3-4.

the prism slowly, we can determine the component colors of the spectrum of a flame or an arc (a bright-line spectrum).

Another device for analyzing spectra is the **grating spectroscope**. A grating is made by carefully scratching regular parallel lines on a

polished surface. A beam of light falling on such a surface is diffracted to produce a spectrum as shown in Fig. 3-3.

Prism and grating spectroscopes are used to analyze, not only visible radiation, but also invisible radiation of wavelengths either longer or shorter than visible radiation. Photographic film or electronic detectors are used to make permanent records of spectral patterns that can then be studied in detail. The visible arc emission spectra of the five elements drawn in Fig. 3-5 are similar to color photographs made with a grating spectroscope.

Emission spectra have played important roles in scientific investigations, for the spectrum of a given element is as individual as a fingerprint. The elements rubidium, cesium, thallium, indium, gallium, and scandium were discovered (between 1860 and 1879) as a result of spectroscopic examination of minerals that revealed spectral lines unlike those of any previously known elements.

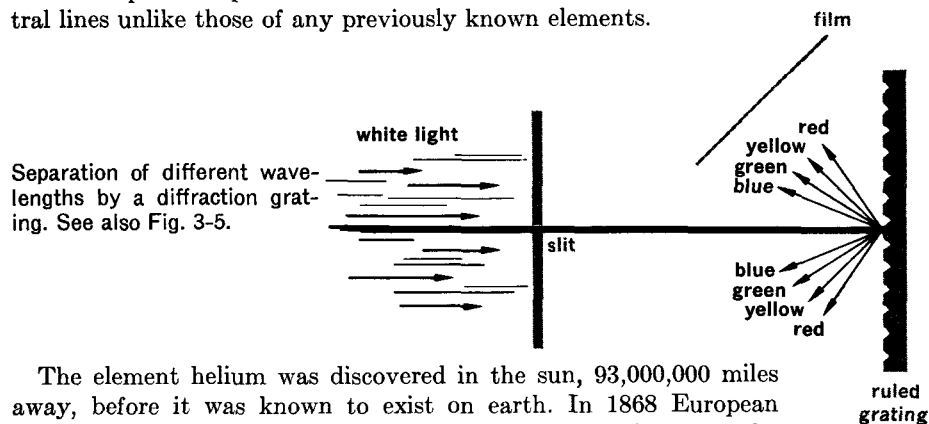


FIG. 3-3

The element helium was discovered in the sun, 93,000,000 miles away, before it was known to exist on earth. In 1868 European astronomers traveled to India to be in a good location to make observations during an eclipse of the sun. A French astronomer, Pierre Janssen, noted some unidentifiable lines in the spectrum of the sun's corona, whereupon one of his English contemporaries, J. N. Lockyer, suggested that these lines might belong to an element that existed in the sun but had never been found on earth. The unknown element was named *helium* from the Greek word *helios* (sun). It was not until twenty-seven years later, in 1895, that Sir William Ramsay discovered that helium did exist on the earth in association with certain minerals. On heating these minerals he found that gases were evolved, one of which had a spectral pattern that matched the pattern discovered by Janssen and Lockyer.

**Absorption Spectra.** At very high temperatures most solids become "white-hot," emitting radiation of all visible wavelengths. Such a radiation is said to give a *continuous emission spectrum* because no absence of color (dark spaces) can be detected when the light is analyzed with a spectroscope. See Fig. 3-5(1). Elements and compounds with high melting points can be used as convenient sources

FIG. 3-4 (Top of facing page.) When a beam of white light (from the projector at the left) passes through a glass prism, the path of the light is bent from the original path. Because light of short wavelength (blue) is bent more than light of long wavelength (red), the beam of white light is spread out as a *spectrum*. In this case the spectrum is continuous (there are no dark areas), showing that this white light is made up of all visible wavelengths (colors).

FIG. 3-5 (Bottom of facing page.) (1) A continuous spectrum from an incandescent solid, obtained with a diffraction grating. (2) The sun's spectrum, showing several dark (Fraunhofer) lines. Also shown are the discontinuous emission spectra of sodium, hydrogen, calcium, mercury, and neon.

of continuous spectra. Tungsten, commonly used as a filament material in incandescent lights, is an example of such an element.

When continuous electromagnetic radiation, for example, white light, passes through a substance, certain wavelengths of radiation may be absorbed. These wavelengths are characteristic of the substance that absorbs the radiation, and the pattern of these dark lines is referred to as an *absorption spectrum*. When cool, a substance absorbs radiation of the same wavelengths that it emits when excited.

Part of the continuous spectrum emitted by the sun is absorbed by the gases in the sun's atmosphere. Because of this, there are narrow dark lines, called Fraunhofer lines after their discoverer, in the otherwise continuous spectrum that reaches us, and the position of these dark spots enables us to identify the gases that absorbed this light. See Fig. 3-5(2).

Study of the absorption spectra of gases has led to the development of methods for testing unknown substances, regardless of whether they are gaseous, liquid, or solid. Transparent colored materials absorb certain wavelengths of visible light. Materials that do not absorb visible light may absorb characteristic wavelengths of ultraviolet or infrared radiation. Modern electronic devices are used to record the absorption spectra automatically (Fig. 3-6). The

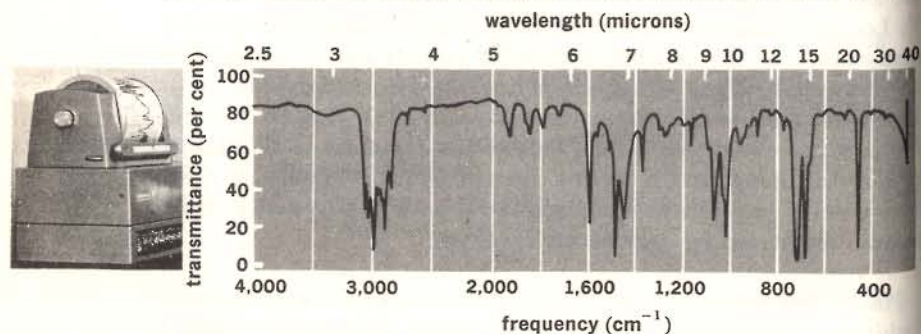
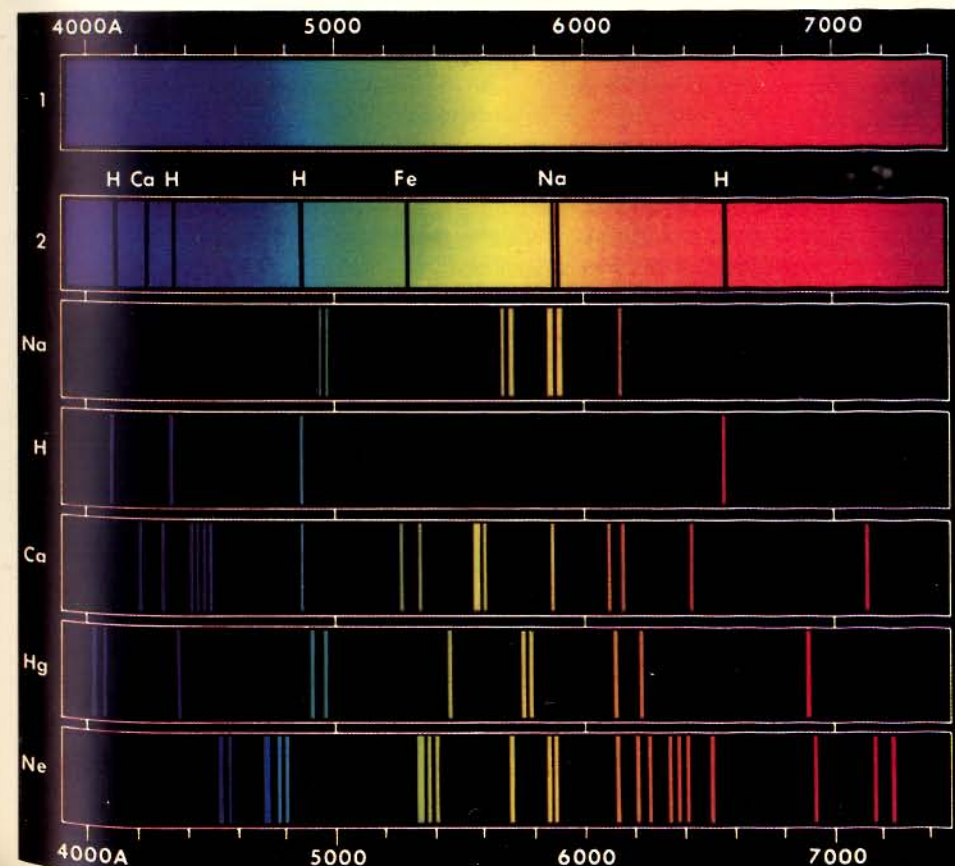
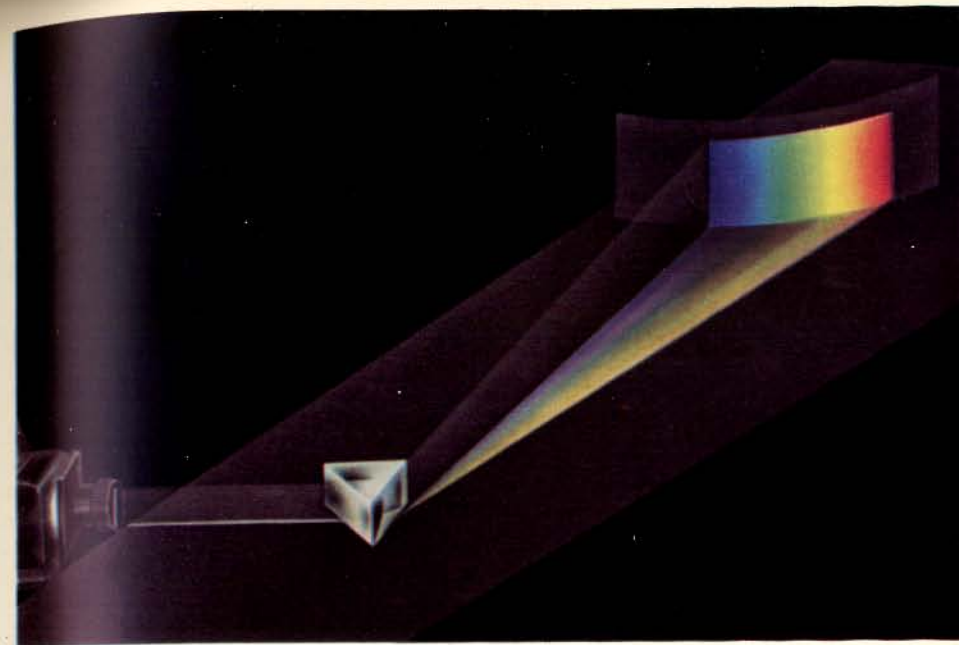


FIG. 3-6 An electronic device automatically records an absorption spectrum (left). The recorded spectrum shown, unrolled and removed from the machine, is the absorption spectrum of toluene. The sharp dips in the curve indicate the wavelengths of radiant energy which have been absorbed most completely. (Courtesy of Perkin-Elmer Corporation, Norwalk, Conn.)





pattern of absorption of radiant energy by a material gives an almost certain indication of the substances, elements or compounds, in the material.

## BOHR'S EXPLANATION OF ATOMIC SPECTRA

When properly excited, samples of the same element always emit the same wavelengths or frequencies of radiation (emission spectrum). Bohr, in 1913, suggested that normally electrons are in places of relatively low energy, called ground states; when the atoms are subjected to high temperature or to bombardment by other electrons, as in an electric arc, the electrons, especially the outer ones in the bombarded atoms, absorb energy and are forced out to places of higher energy, or to excited states. When the excited electrons fall back to lower energy levels, a certain amount of radiant energy is given off, the amount of energy determining the wavelength of the radiation.

In 1900 Max Planck described radiant energy as consisting of units of energy or *quanta*. According to Planck, the energy of a quantum is proportional to the frequency  $\nu$  of the radiation,  $E = h\nu$ , where  $h$  is called *Planck's constant of proportionality*. Bohr reasoned that, when electrons in atoms gained energy, they were excited to definite levels of higher energy,  $E_H$ ; and that, when the electrons lost energy, they fell back to definite levels of lower energy,  $E_L$ . For two given levels, the difference in energy,  $E_H - E_L$ , would be constant for all atoms of the same kind and thus explain the fact that the radiant energies emitted by a given element always have the same frequencies (or wavelengths). That is,  $E_H - E_L = \Delta E = h\nu$ .

The spectrum of hydrogen was analyzed in detail by Bohr. Not only did he examine the four lines in the visible spectrum shown in Fig. 3-5, and some other visible lines correlated mathematically by the physicist J. J. Balmer, but he also studied lower energy lines in the infrared, discovered by F. Paschen. According to Bohr, the Balmer lines resulted from electrons falling a great distance into a lower energy level, and the Paschen lines resulted from shorter falls into a higher energy level.

One of Bohr's great achievements was the development of a theory which not only accounted for the known Balmer and Paschen lines but which enabled him to predict the existence of unsuspected spectral lines such as the Lyman series of lines. In Fig. 3-7 these three series of lines are related to theoretical changes in energy levels. The energy levels are numbered 1, 2, 3, 4 . . . , 1 being the lowest or ground-state level. Of the three series shown, the Lyman radiations, arising from electrons falling into the energy level closest to the positive nucleus, have the shortest wavelengths; the Paschen radiations have the longest. Within each series, the greater the difference in energy levels, the shorter the wavelength of the emitted radiation.



# ELECTRONIC STRUCTURE OF ATOMS

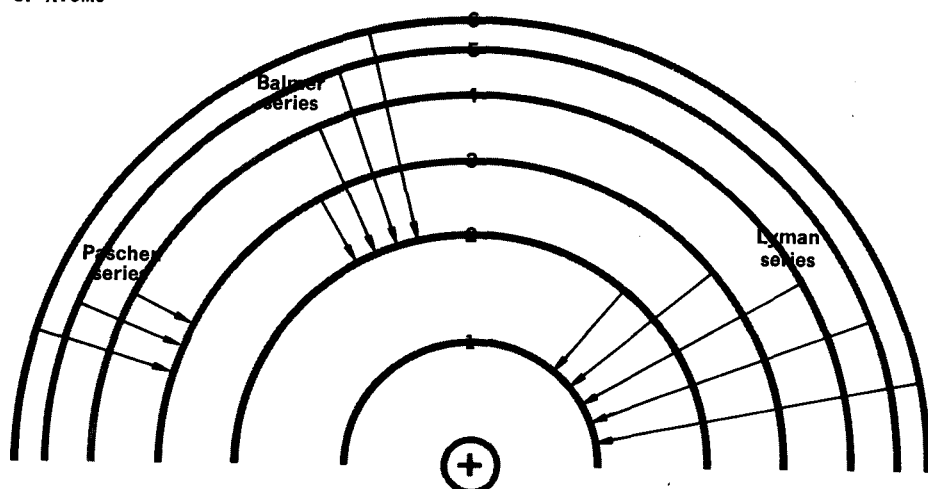


FIG. 3-7 Electron jumps account for the different lines in the hydrogen emission spectrum.

**BOHR ATOM.** As a result of Bohr's work, the atom came to be visualized as a positive nucleus surrounded by one or more electrons traveling in definite orbits. So long as an electron remained in a given orbit, it neither gained nor lost energy. An electron in an atom could gain or lose energy only by absorbing or emitting a quantum or unit amount of energy, in which event it jumped to a higher or lower orbit. This model of atomic structure rapidly gained favor, because it was useful in explaining many observations and in making predictions and calculations. In addition to accounting for atomic spectra, Bohr's model and the mathematical relations that he developed helped explain the properties of X rays, enabled the calculation of ionization energies, and provided a better understanding of sources of radiant energy in general. Some of these topics are taken up in the following sections.

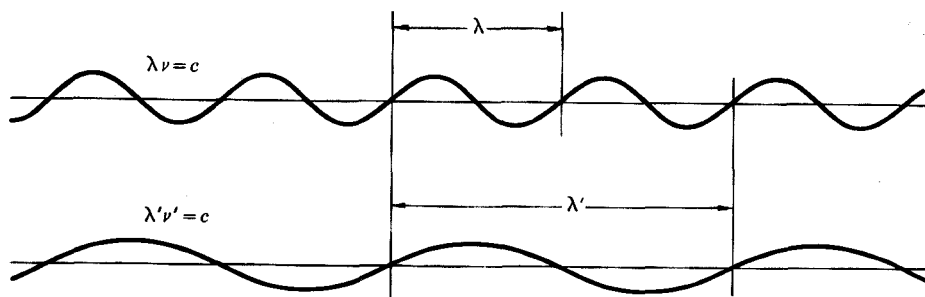


FIG. 3-8 Radiant energy can be thought of as a wave train traveling in a straight line at the speed of light  $c$ . The frequency  $\nu$  is the number of waves that pass a given point per second. The wavelength  $\lambda$  is inversely proportional to the frequency; if the wavelength is doubled, the frequency is halved.

**Energy of Electromagnetic Radiation.** Visible light is one of the types of electromagnetic radiation described in Table 3-1. All types travel at the speed of light ( $c$ ),  $3.00 \times 10^{10}$  cm/sec but differ in wavelength ( $\lambda$ ) or frequency ( $\nu$ ). See Fig. 3-8. Knowing the wavelength of a radiation, we can calculate its frequency by using the relation  $\lambda\nu = c$ . Taking the red Balmer line of hydrogen as an example,

$$\lambda = 6563 \text{ \AA} \text{ or } 6.563 \times 10^{-5} \text{ cm}$$

$$\begin{aligned}\nu &= \frac{c}{\lambda} = \frac{3.00 \times 10^{10} \text{ cm/sec}}{6.563 \times 10^{-5} \text{ cm}} \\ &= 4.57 \times 10^{14} \text{ sec}^{-1}\end{aligned}$$

### Electromagnetic radiation

TABLE 3-1

name	approximate wavelength	frequency, photons/sec	energy per photon, ev	source
radio, TV	$2 \times 10^6 \text{ cm}$	$1.5 \times 10^4$	$6.2 \times 10^{-11}$	oscillating electric circuits
short Hertzian, radar	$4 \times 10^3 \text{ cm}$	$7.5 \times 10^6$	$3.1 \times 10^{-8}$	
infrared, or heat	$3.3 \times 10^{-2} \text{ cm}$	$9 \times 10^{11}$	$3.7 \times 10^{-3}$	
visible light	$7 \times 10^{-5} \text{ cm}$	$4.3 \times 10^{14}$	1.8	vibrating molecules and atoms
ultraviolet	$4 \times 10^{-5} \text{ cm}$	$7.5 \times 10^{14}$	3.1	
extreme ultraviolet	$1.2 \times 10^{-6} \text{ cm}$	$2.5 \times 10^{16}$	$1.0 \times 10^1$	vibrating electrons in atoms
X rays	$5 \times 10^{-7} \text{ cm}$	$6 \times 10^{16}$	$2.5 \times 10^2$	
gamma rays	$1.2 \times 10^{-9} \text{ cm}$	$2.5 \times 10^{19}$	$1.0 \times 10^5$	
cosmic rays	$1 \times 10^{-12} \text{ cm}$	$3 \times 10^{22}$	$1.2 \times 10^8$	nuclear changes
	$1 \times 10^{-13} \text{ cm}$	$3 \times 10^{23}$	$1.2 \times 10^9$	nuclear changes (?)

Radiant energy is a form of energy that consists of electromagnetic waves traveling outward from a source. Some of the common kinds of electromagnetic radiation are radio waves, infrared rays, visible light, and X rays. The velocity at which these radiations travel is  $3 \times 10^{10}$  cm (186,000 miles) per second in a vacuum.

The most characteristic property of radiant energy is its frequency. The distance between similar phases of the radiation is called its wavelength. The great precision with which radiation can be measured has led to the standard meter being defined as 1,650,763.73 wavelengths of the orange-red line of krypton-86. This supercedes the standard meter as marked on the platinum-iridium bar mentioned in Chap. 1.

The greater the frequency of the radiant energy, the shorter the wavelength, and the greater the energy of the radiation. According to the quantum theory, radiation can be thought of as a series of energy packets or photons. The energy of a radiation photon is directly proportional to the frequency of that radiation.

The energy associated with a single quantum or photon of radiant energy can be calculated from Planck's relationship,  $E = h\nu$ , with  $h$  having the value of  $6.63 \times 10^{-27}$  erg sec/photon.<sup>1</sup> For the red Balmer line of hydrogen,

$$\begin{aligned} E &= (6.63 \times 10^{-27} \text{ erg sec/photon}) (4.57 \times 10^{14} \text{ sec}^{-1}) \\ &= 3.03 \times 10^{-12} \text{ erg/photon} \end{aligned}$$

The energy of each photon or *quantum* of this red light is  $3.03 \times 10^{-12}$  erg. As the equation  $E = h\nu$  indicates, the greater the frequency, the greater the energy associated with a quantum of radiation. In Table 3-1 it is shown that electron changes in atoms are sources of radiation that range in frequency from visible light to X rays. One source of lower-frequency (lower-energy) electromagnetic radiation is an oscillating electric circuit; a source of higher-frequency (higher-energy) is a change in the nucleus of an atom.

**Electron Jumps and Radiant Energy.** Consider the red Balmer radiation just described. Bohr's idea was that the energy of one photon,  $3.03 \times 10^{-12}$  erg, must be the difference in energy between two energy levels in the hydrogen atom, such that  $E_H - E_L = \Delta E = h\nu = 3.03 \times 10^{-12}$  erg. He developed an equation that related the frequency of a line in the hydrogen spectrum to the numbers of the two energy levels involved in the jump of an electron:

$$\nu = \frac{2\pi^2 me^4}{h^3} \left( \frac{1}{n_L^2} - \frac{1}{n_H^2} \right)$$

The frequency of the emission line is  $\nu$ ,  $m$  is the mass of the electron,  $e$  is the charge on the electron,  $h$  is Planck's constant,  $n_L$  is the number of the lower energy level into which the electron falls, and  $n_H$  is the number of the higher level from which the electron falls. (The numbers  $n_L$  and  $n_H$  are the *first* quantum numbers, described in Table 3-2.) In Bohr's words:<sup>2</sup>

We see that this expression accounts for the law connecting the lines in the spectrum of hydrogen. If we put  $n_L = 2$  and let  $n_H$  vary, we get the ordinary Balmer series. If we put  $n_L = 3$ , we get the series in the ultra-red observed by Paschen and previously suspected by Ritz. If we put  $n_L = 1 \dots$ , we get [a] series ... in the extreme ultraviolet ... which [is] ... not observed, but the existence of which may be expected.

Specifically, in solving the equation above for the Balmer lines in Fig. 3-5, we find that for the fall of an electron from  $n_H = 3$  to  $n_L = 2$  the calculated frequency corresponds to the red line at a wavelength of 6,563 Å; for the fall from  $n_H = 4$  to  $n_L = 2$  the frequency corre-

<sup>1</sup> Generally  $\nu$  is expressed simply as a number per second, having the unit of reciprocal seconds, for example,  $4.57 \times 10^{14}$ /sec or  $4.57 \times 10^{14} \text{ sec}^{-1}$ . Generally  $\lambda$  is expressed simply in units of length, with the "per wave" understood. The common units for  $h$  are erg sec; we use erg sec/photon here to emphasize that Planck's quantum of action is associated with each packet of radiant energy.

<sup>2</sup> N. Bohr, *Philosophical Magazine*, **26**: 1 (1913).

sponds to the green line at 4,861 Å; the fall from  $n_H = 5$  to  $n_L = 2$ , to the violet line at 4,340 Å; and so on. With a fine spectroscope it is possible to observe 12 Balmer lines, all at frequencies consistent with Bohr's formula.

Perhaps the most striking part of Bohr's quoted paragraph is his prediction that undiscovered lines probably exist in the ultraviolet. For example, using  $n_L = 1$  and  $n_H = 6$  in the equation, it is calculated that a line should occur at 938 Å, much too short a wavelength to see with the eye. The series of ultraviolet lines predicted by Bohr, by setting  $n_L = 1$  and letting  $n_H$  vary, was sought and found by T. Lyman at Princeton in 1916, thus crowning the theory with success.

**Ionization Energies.** The work of Franck and Hertz on ionization energies, mentioned in Chap. 2, actually followed the first work on atomic spectra and was carried out in part as a test of the Bohr theory. However, at the time that Bohr developed his theory, the ionization energy of hydrogen was experimentally known to be 13.54 ev. From his model of a hydrogen atom with the electron in a definite energy level near the oppositely charged nucleus, and using Planck's constant, Bohr calculated the theoretical ionization energy of hydrogen to be 13 ev. This close check with the experimental value gave many persons confidence in Bohr's theory.

With Bohr's formula and more recent data than he had in 1913 for Planck's constant and for the charge and mass of the electron, we can calculate a modern value for the ionization energy of hydrogen. To do this, we consider the energy involved in the fall of an electron from an infinitely high energy level,  $n_H = \infty$ , to the lowest or ground-state level,  $n_L = 1$ . The energy involved in this exothermic process is numerically equal to the energy required in the endothermic process of exciting an electron from the ground state to an infinite distance from the nucleus, that is, the energy necessary to ionize a hydrogen atom.

Using the equation for calculating the frequency, letting  $n_L = 1$  and  $n_H = \infty$ , we find, for the fall of an electron from infinity into the lowest energy level of hydrogen,

$$\nu = \frac{2\pi^2 me^4}{h^3} \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right) = \frac{2\pi^2 me^4}{h^3}$$

Substituting values for the mass and charge<sup>1</sup> of the electron given in Chap. 1, we have

$$\begin{aligned}\nu &= \frac{2(3.14)^2 (9.11 \times 10^{-28} \text{ g}) (4.80 \times 10^{-10} \text{ esu})^4}{(6.63 \times 10^{-27} \text{ erg sec})^3} \\ \nu &= 3.27 \times 10^{15} \text{ sec}^{-1}\end{aligned}$$

Then, relating the frequency of the radiation to its energy in ergs

<sup>1</sup> The term esu has the units of  $(\text{cm}^{3/2} \text{ g}^{1/2} \text{ sec}^{-1})$  in the cgs system.

( $E = h\nu$ ) and converting ergs to electron volts with the factor  $1 \text{ ev} = 1.6 \times 10^{-12} \text{ erg}$ , we calculate

$$E = (6.63 \times 10^{-27} \text{ erg sec}) (3.27 \times 10^{15} \text{ sec}^{-1}) \left( \frac{1 \text{ ev}}{1.60 \times 10^{-12} \text{ erg}} \right) \\ = 13.6 \text{ ev/photon}$$

as the energy of the radiation necessary to ionize a hydrogen atom.

By using more significant figures in the values for the constants, a more precise check with the modern value for hydrogen given in Table 2-4 can be achieved.

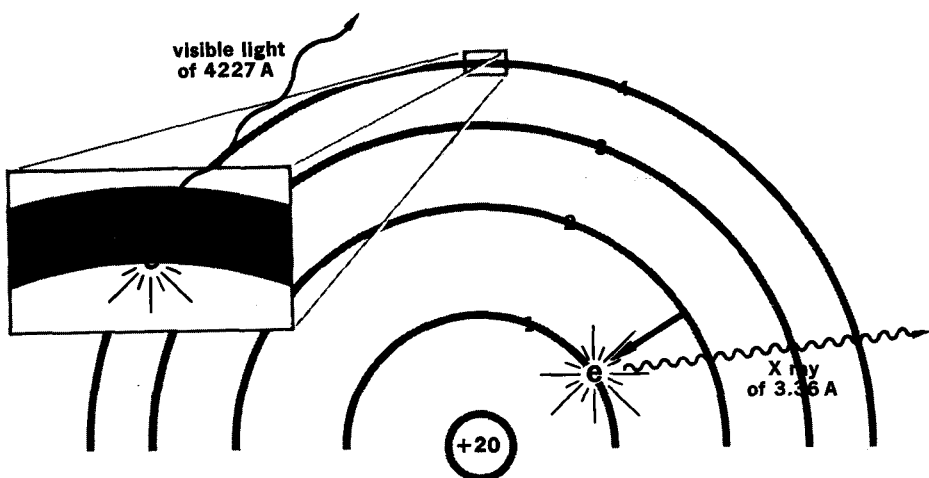
Calculations of ionization energies for atoms more complex than hydrogen can be made. It is interesting to note that the energies of radiations necessary to ionize atoms are considerably greater than those associated with visible light. The visible spectrum involves a range of about 1.8 to 3.1 ev per quantum, as shown in Table 3-1. These values can be compared with the ionization energies listed in Table 2-4.

Since wavelength and energy are interrelated, spectra can be used to determine temperatures. For example, in the spectra of certain stars the line in the extreme ultraviolet associated with the fourth ionization energy of neon (97 ev) has been detected. Using the conversion factor of  $1.16 \times 10^4 \text{ }^\circ\text{K/ev}$ , we calculate that, in order to excite four electrons from neon atoms, the atmospheric temperature of such stars must be over 1 million  $^\circ\text{K}$ .

**X rays.** In Chap. 2 Moseley's study of the wavelengths of X rays was described. The cathode-ray bombardment of an element gives rise to X rays when electrons that are strongly held are knocked out of atoms and other electrons fall in to fill the vacancies. The nuclei of the lightest atoms do not attract electrons sufficiently to produce X rays; in the case of hydrogen, the highest energy radiation measured has too great a wavelength ( $9.17 \times 10^{-6} \text{ cm}$ ) to be in the X-ray range. But for atoms whose nuclei have a great enough positive charge, the fall of an electron to an inner level gives rise to a photon of X radiation. The highest-energy X rays, those studied by Moseley, involve electrons that fall into vacancies in energy level 1. The production of visible light as compared with X radiation is shown schematically in Fig. 3-9.

## ENERGY SUBLEVELS

In the early days of the study of electron energy levels, the Bohr atom was often described as a tiny solar system, with the nucleus as the sun surrounded by the planetary electrons in various orbits, designated K, L, M, N, etc., or 1, 2, 3, 4, etc. Continuing study, however, brought fundamental changes in theory, so that the theoretical atom of today differs from the early Bohr atom as much as that atom differed from the first Rutherford atom. More precise and



When excited electrons fall from higher energy levels to lower levels, radiant energy is emitted. Falls into vacancies in the first energy level result in the emission of X rays, except for elements with very low nuclear charges. Falls into intermediate levels may result in the emission of visible light.

FIG. 3-9

sensitive photographic measurements of the radiations emitted by excited atoms revealed that the energies of electrons within a given main energy level differed from one another. It became necessary to postulate that within a main energy level there must be energy sublevels to account for the large number of wavelengths of radiant energy emitted by excited atoms. Also, the concept of energy sublevels arose as a result of study of the periodic table. Some complicated arrangement of electrons within main levels was called for to account for the existence of the A and B families and the difference in the lengths of the periods: only 2 elements in the period 1, 8 each in periods 2 and 3, 18 each in the longer periods 4 and 5, and 32 in the very long period 6. It seemed clear that the number of electrons possible in the higher energy levels must be greater than in the lower levels.

Recognition of the various groups of spectral lines corresponding to sublevels did not occur all at once, but rather it comprised a series of discoveries in the early years of this century. The sublevels were given names suggested as each new series of lines in the spectra was discovered: *sharp*, *principal*, *diffuse*, and *fundamental*. Today we speak of these energy sublevels as the *s*, *p*, *d*, and *f* sublevels, respectively.

The number of sublevels in a main energy level is apparently equal to the number of that level. That is, in the first main level there is only one energy level, in the second main level there can be two energy sublevels, in the third main level there can be three energy

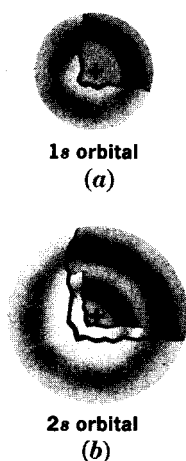
sublevels, etc. To say it another way, in the first main level there is only the  $s$  sublevel, in the second there can be  $s$  and  $p$  sublevels, in the third there can be  $s$ ,  $p$ , and  $d$  sublevels, etc. See Fig. 3-9.

### ATOMIC ORBITAL AND QUANTUM NUMBERS

A popular theory today describes the electrons in a sublevel as in constant motion, with this motion limited to regions of space called **orbitals**. An electron may be in any place within an orbital at a given time, although it tends to occupy certain portions of its orbital to a greater extent than other portions. No more than two electrons may occupy each orbital.<sup>1</sup> Magnetic studies indicate that electrons act as if they were spinning and that two electrons in the same orbital must be spinning in opposite directions.

The first energy level (the K or 1 level) contains only one orbital; therefore, this main level can contain no more than two electrons. (Also, because this simplest main level is limited to two electrons, it is not, strictly speaking, divided into sublevels; "the  $1s$  sublevel" and the "first energy level" are merely different ways of referring to the same energy level.) The shape of the orbital occupied by these two electrons is believed to be spherical with the nucleus at the

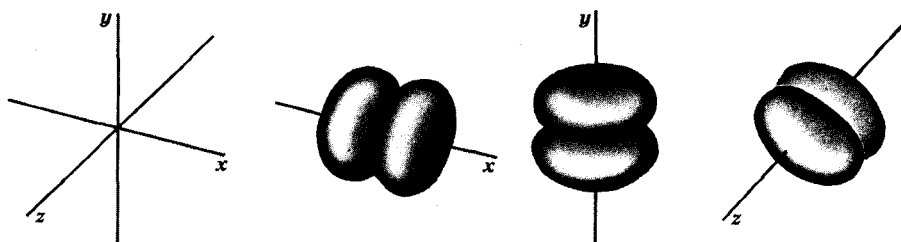
Schematic representation of  $s$  orbitals. Note that the  $1s$  orbital has one region of high electron density (more deeply colored region), but that the  $2s$  orbital has two such regions. The nucleus is relatively small and may be considered to be at the center of the (+).



**FIG. 3-10**

center (Fig. 3-10a). The orbitals of  $s$  sublevels have spherical shapes and are called  $s$  orbitals.

The second main energy level, with a maximum of eight electrons, consists of four orbitals. One of these is an  $s$  orbital, that is, spherical (Fig. 3-10b). The other three orbitals are dumbbell-shaped (Fig. 3-11)



**FIG. 3-11**

A representation of each of the three  $2p$  orbitals. To visualize an atom, imagine that these three orbitals are put together with each axis perpendicular to the other two. The nucleus of the atom is then located at the intersection of  $x$ ,  $y$ , and  $z$  coordinates. Other orbitals, for example,  $s$ , may interpenetrate these  $p$  orbital clouds.

<sup>1</sup> Although there is only one electron in an orbital, this electron acts as if it occupied the whole region available to the orbital. Just one electron can be thought of as an electron "cloud" that has a high probability of occupying some region of space about a nucleus.

and are called *p* orbitals. Thus, the second main level consists of two sublevels, the *2s* sublevel and the *2p* sublevel; the *2s* sublevel consists of a single *s* orbital, and the *2p* sublevel consists of three *p* orbitals.

The third main energy level, with a maximum of 18 electrons, contains three sublevels consisting of nine orbitals: one *s* orbital, three *p* orbitals, and five *d* orbitals. The fourth main energy level, consisting of four sublevels, contains 16 orbitals: one *s*, three *p*, five *d*, and seven *f* orbitals.<sup>1</sup> The *d* and *f* orbitals are thought to have more complicated shapes than the *s* and *p* orbitals.

To summarize:

### *Subdivision of main energy levels*

TABLE 3-2

main energy level	1	2	3	4
number of sublevels ( <i>n</i> )	1	2	3	4
number of orbitals ( <i>n</i> <sup>2</sup> )	1	4	9	16
kind and number of orbitals	<i>s</i> 1	<i>s</i> <i>p</i> 1 3	<i>s</i> <i>p</i> <i>d</i> 1 3 5	<i>s</i> <i>p</i> <i>d</i> <i>f</i> 1 3 5 7
maximum number of electrons	2	2 6	2 6 10	2 6 10 14
total maximum number of electrons ( <i>2n</i> <sup>2</sup> )	2	8	18	32

All these details of sublevels and orbitals have been worked out mainly on the basis of study of the radiant energy emitted by excited atoms. One of the fundamental theories of matter and energy is that energy can be emitted only in definite units or quanta. Out of Max Planck's quantum theory of matter and energy has come a description of atomic structure that represents each electron in a given atom in terms of four quantum numbers. The details of the quantum theory are beyond the scope of this book, but qualitatively these numbers can be described as follows for a given electron:

The *first quantum number* tells which main level the electron occupies (1, 2, or 3, etc.).

The *second quantum number* tells which sublevel the electron occupies, that is, the shape of the electron cloud that the electron patrols (*s*, *p*, or *d*, etc.).

The *third quantum number* tells which orbital the electron occupies within a sublevel.

The *fourth quantum number* describes the direction of the electron's spin.

In a certain atom, therefore, each electron in its unexcited state (ground state) is described by *four quantum numbers*. No two electrons in the same atom can have the same four quantum numbers. This is the famous Pauli exclusion principle, named for Wolfgang Pauli.

<sup>1</sup> There are also *g*, *h*, *i*, etc., sublevels, which may be occupied by electrons that have been excited or activated; however, the outermost *ground-state sublevels* that are occupied in the most complicated atoms known today are the *7s*, *6d*, and *5f* sublevels.



# ELECTRONIC STRUCTURE OF ATOMS

1. The main energy levels have number designations of 1, 2, 3, 4, 5, 6, 7.
2. The number of sublevels within a main level is numerically equal to the number designation of that level.
3. The square of the number designation of a main energy level gives the number of orbitals in that level.
4. The number of orbitals multiplied by 2 gives the maximum number of electrons in a main energy level.

Table 3-2 shows how these statements apply to the first four main levels.

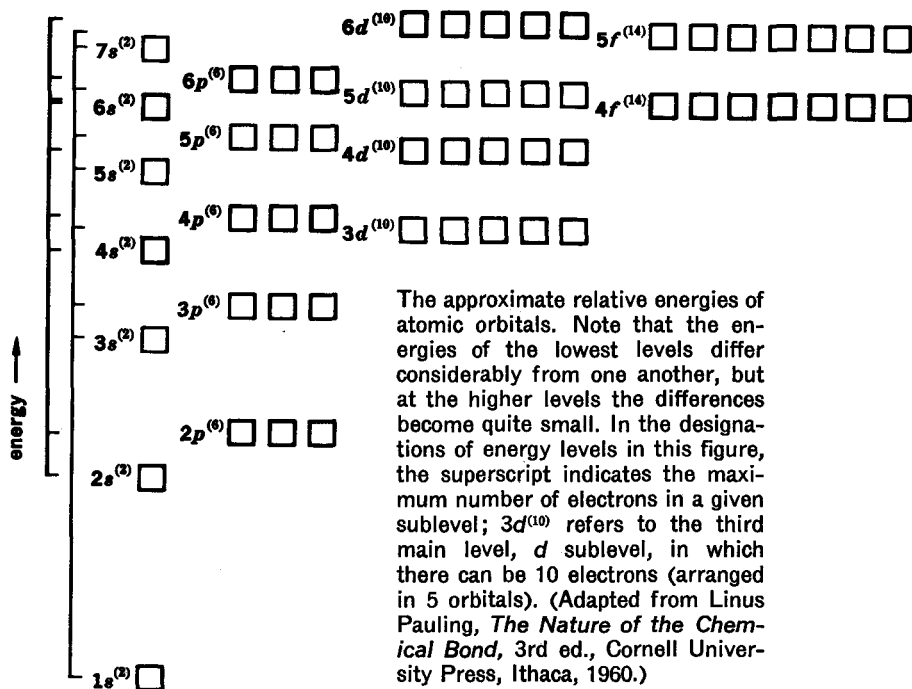


FIG. 3-12

**Order of Filling Orbitals.** The first two main energy levels are widely separated in energy value, but for the third, fourth, fifth, and higher main levels there can be overlapping of energies. For example, as the atomic number increases, the  $5s$  sublevel is added to before the  $4d$  and  $4f$  sublevels.

The sublevels may be listed in order of increasing energy as follows:  $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p$ . This order is shown schematically in Fig. 3-12, a small box indicating each orbital in a sublevel. Figure 3-13 is useful in helping one remember the order of increasing energies.

# ELECTRONIC STRUCTURE OF ATOMS

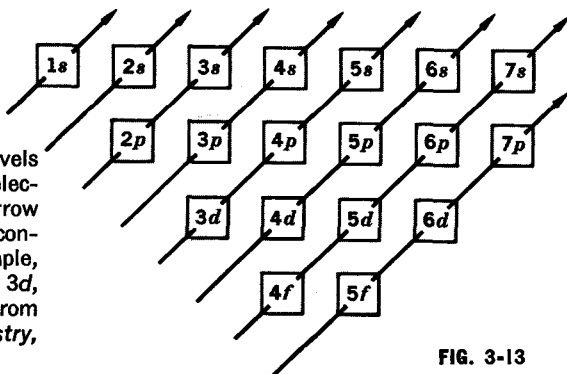
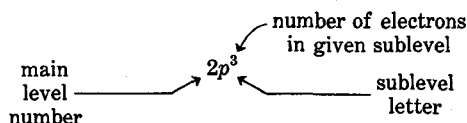


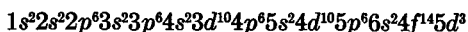
FIG. 3-13

The approximate order in which sublevels are filled with increasing numbers of electrons. Follow through each slanting arrow in turn, starting with the lowest and continuing with the next higher. For example, after 3s is filled, there follow 3p, 4s, 3d, 4p, etc. (Adapted with permission from Therald Moeller, *Inorganic Chemistry*, John Wiley & Sons, Inc., 1952.)

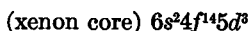
As the number of electrons increases, from atom to atom in the periodic table, two general principles govern the order in which the sublevels and orbitals in the different energy levels are filled. (1) The order in which sublevels are filled usually follows the energy ranking, as shown in Fig. 3-13, starting with the sublevel lowest in energy and working up. (2) Within a given sublevel, each orbital is usually occupied by a single electron before any orbital has two electrons.<sup>1</sup> Although there are exceptions to the order in which orbitals are filled, these two principles apply in enough cases to make them reliable guides. The application of these principles to twelve elements is shown in Table 3-3; each arrow represents an electron. The following convention is used to summarize the number and location of electrons in atoms conveniently:



To illustrate a rather complicated case, we can apply these principles to element 73, tantalum. There are 73 electrons to be accounted for. Following the scheme used in Figs. 3-12 and 3-13, we find the following electronic configuration for tantalum:



Or it can be abbreviated as



This agrees with the configuration given for element 73 in the periodic table inside the front cover. The term "xenon core" stands for the electron arrangement of xenon, element 54; it indicates the filling of all sublevels through 5p<sup>6</sup>. Summing up, the number of electrons per main energy level for tantalum is 2, 8, 18, 32, 11, 2.

<sup>1</sup> This rule for the filling of orbitals is known as Hund's *principle of maximum multiplicity*.

# ELECTRONIC STRUCTURE OF ATOMS

Group IA IIA

Period 1





	3	4
2		
3	11	12
4	19	20
5	37	38
6	55	56
7	87	88




The order in which orbitals are filled is related to the organization of the periodic table.


The electronic structure of an atom as determined experimentally does not always agree with that predicted by the use of the scheme pictured in Fig. 3-13. Chromium, Cr, for example, according to its spectrum has the structure (argon core)  $4s^1 3d^5$ ; however, according


TABLE 3-3 *Electron arrangements*

main levels 1		2				3	summary
sublevels	s	s	p			s	
H	↓						$1s^1$
He	↑↓						$1s^2$
Li	↑↓	↓					$1s^2 2s^1$
Be	↑↓	↑↓					$1s^2 2s^2$
B	↑↓	↑↓	↓	□	□		$1s^2 2s^2 2p^1$
C	↑↓	↑↓	↓	↓	□		$1s^2 2s^2 2p^2$
N	↑↓	↑↓	↓	↓	↓		$1s^2 2s^2 2p^3$
O	↑↓	↑↓	↑↓	↓	↓		$1s^2 2s^2 2p^4$
F	↑↓	↑↓	↑↓	↑↓	↓		$1s^2 2s^2 2p^5$
Ne	↑↓	↑↓	↑↓	↑↓	↑↓		$1s^2 2s^2 2p^6$
Na	↑↓	↑↓	↑↓	↑↓	↑↓	↓	$1s^2 2s^2 2p^6 3s^1$
Mg	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	$1s^2 2s^2 2p^6 3s^2$

IIIB	IVB	VB	VIB	VIIIB	VIIIIB	IB	IIIB			
21	22	23	24	25	26	27	28	29	30	
										
39	40	41*	42	43*	44*	45*	46*	47	48	
										
57	58-71	72	73	74*	75	76	77	78*	79	80
										
89	90-103	104								
										

31	32	33	34	35	36
					
49	50	51	52	53	54
					
81	82	83	84	85	86
					

58	59	60*	61	62	63	64	65	66	67	68	69	70	71
													

90	91	92	93	94	95	96	97	98	99	100	101	102	103
													

to the regular prediction, its expected structure would be (argon core)  $4s^2 3d^4$ . There is a further word about such irregular behavior in Chap. 17. It is sufficient at this time for us to learn how to make regular predictions and to recognize that exceptions to the rule do exist.

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enough elements are ever found or synthesized, period 7 will contain 32 elements, also.

A third important feature to note is that each period, except the first, ends with the filling of a  $p$  sublevel. The elements in group VIIIA are called the noble gases because they are gaseous at room temperature and because they have little tendency to react chemically with other elements. Only a few compounds of them have been made. Their extreme inactivity is evidently related to their electronic structures, a topic discussed more fully in Chap. 4.

**Orbitals and Ionization Energies.** In Table 2-4 and Fig. 2-16 we noted the periodic character of changes in the first ionization energies of elements. We can understand some of the variations from ideal periodic behavior within each major period by examining the changes in energy as related to the arrangement of electrons in orbitals and sublevels.

In Fig. 2-16 it is seen that the first electron is knocked off a boron atom (B), atomic number 5, more easily than off the previous atom (beryllium); the same behavior is shown by aluminum (number 13) following magnesium. A glance at Fig. 3-14 shows that both elements 5 and 13 are in family IIIA, in which the first of the six  $p$  electrons in a sublevel is added. This first  $p$  electron is in a new sublevel; it is somewhat less strongly held than the previous electron. Examination of Fig. 2-16 indicates that this same behavior is shown by elements 31, 49, and 81 (gallium, indium, and thallium), which are also in family IIIA and which have but one  $p$  electron in a new sublevel.

Dips in the graph in Fig. 2-16 show that a somewhat lower ionization energy than expected is found for oxygen (8), sulfur (16), selenium (34), and tellurium (52). This is apparently associated with the pairing of  $p$  electrons in orbitals. As shown in Table 3-3, when electrons are added within a sublevel, one electron is added to each orbital before a second is added to any orbital. In each element in family VIA, as for oxygen in Table 3-3, a fourth  $p$  electron is added to make a pair of electrons in one orbital. Probably owing to the repulsion between two electrons close to one another, this second electron in an orbital is less strongly held, so that the ionization energy needed to remove it is less than would be predicted. In Fig. 2-16, the elements boron, carbon, and nitrogen lie on one smooth line, and the elements oxygen, fluorine, and neon on another. The members of the second set, in which  $p$  orbital electrons are being paired, have lower ionization energies than predicted on the basis of the first set.

To summarize:

1. When a new main outer level is begun with the addition of the first  $s$  electron, this electron is relatively loosely held, and the ionization energy is low.

2. Within a period there is a general increase in ionization energy,

as no new main levels are added and the attractive positive charge on the nucleus increases steadily.

3. The completion of *p* sublevels leads to especially high ionization energies (VIII A family elements); the completion of *s* and *d* sublevels (IIB family elements) is also marked by peaks in ionization energy, as shown in Fig. 2-16.

## GENERAL CONSIDERATIONS ON ELECTRON POSITIONS

As indicated in Fig. 3-12, there is little difference in energy of electrons in different sublevels at higher energies. For example, the 6*s*, 4*f*, and 5*d* sublevels are quite close together. It takes relatively little energy to excite electrons in these outer energy levels to the next higher level.

We must emphasize that in spite of these specific descriptions of the energies of the different electrons and the shapes of the orbitals they patrol—in spite of this apparently very detailed information—the precise location of any electron is not known. We think we know something about the most probable location of electrons in atoms, but there may be a fundamental limitation to our ability to investigate particles as small as electrons. According to Werner Heisenberg's uncertainty principle, it is not possible to determine the position and the velocity of an electron experimentally at the same time. An electron is such a small particle that it is disturbed or set off in some unpredictable motion by an attempt to examine it, say by irradiating it with light or X rays. Although we attempt to determine where the electron is, we cannot determine its position exactly, and we cannot tell where it is going after we observe it. At present it seems appropriate to think of an electron as a sort of charged cloud that occupies a relatively large orbital space in an atom.

It has been argued that, because we cannot predict with certainty how electrons will behave, we can never predict with certainty any future chemical or physical systems. This modern scientific argument for uncertainty is in sharp contrast with the determinism of the past century, which led many to believe that theoretically a person could predict future events if only he knew enough about the chemical and physical systems involved.

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## CHAPTER REVIEW

### *Terms*

Emission and absorption spectra, continuous and discontinuous spectra, flame spectra, prism and grating spectroscopes, quanta,  $\nu$ ,  $\lambda$ ,  $h$ , energy level, Balmer lines, Paschen lines, Lyman lines, Bohr atom, photon, electron jumps, ionization energy, energy sublevels, atomic orbital, *s* orbital, *p* orbital, *d* orbital, *f* orbital, quantum number, Pauli exclusion principle, Hund's principle, xenon core, argon core, Heisenberg's uncertainty principle, electron cloud.

*Exercises*

1. When light emitted by the tungsten filament of a light bulb is analyzed in a spectroscope, a continuous emission spectrum is observed. When the light produced by heating a sodium compound in a flame is analyzed in a spectroscope, a discontinuous emission is observed.
  - a. Why are these two spectra referred to as emission spectra?
  - b. What is the nature of the light coming from the tungsten so that no discontinuities are observed in its spectrum?
  - c. What is the nature of the light coming from the sodium compound so that its spectrum is discontinuous?
  - d. If sodium vapor is placed in the path of the light coming from the incandescent tungsten, how does the resulting spectrum differ from the one first described?
  - e. If sodium vapor is placed in the path of the light coming from the sodium compound, how does what one sees in the spectroscope differ from the first analysis of the sodium light?
2. Sodium and potassium belong to the same family of elements; yet sodium compounds emit a yellow light when heated, and potassium compounds a violet light. How do we account for these differences?
3. We usually describe the light coming from a neon sign as red or orange-red. Yet examination of the emission spectrum of neon (Fig. 3-5) shows lines in the blue, green, and yellow portions of the spectrum as well as in the red. Why do we not see these colors?
4. State in a relative way how the "electron jumps" that give rise to the red lines of the neon spectrum must differ from those which give rise to the green lines.
5. Calcium is believed to be one of the elements present in the sun. On what do we base this belief?
6. In the absorption spectrum of neon, the lines corresponding to the red lines in the emission spectrum are black. Why?
7. Calculate the frequency of ultraviolet radiation of wavelength 3,000 Å; compare with the frequency of radiowaves of  $1 \times 10^{12}$  Å.
8. Calculate the energies of the two radiations described in Exercise 7.
9. What is thought to take place in atoms of hydrogen to give rise to the Balmer series of lines; the Paschen series; the Lyman series?
10. When cesium and platinum are exposed to visible radiation, the former emits electrons, but the latter does not. What kind of information does this observation give about the relative magnitudes of the ionization energies of these metals? Explain.
11. Helium atoms do not emit X rays when bombarded by electrons in a cathode-ray tube. Why?
12. Calculate the energy of a photon of red light with a wavelength of 7,000 Å.

13. What is the wavelength of a photon with twice as much energy as a photon of red light of wavelength 7,000 Å? What is the color of this radiation?
14. What part of sunlight is most damaging to skin? Why?
15. Suggest a reason why photographic film is more sensitive to direct sunlight than to reflected sunlight.
16. Specifically, what do we mean when we speak of main energy levels in an atom? Summarize the evidence that supports this concept.
17. Why is it necessary to postulate energy sublevels?
18. What is an atomic orbital? Describe the shapes of the 2s orbital and 2p orbital.
19. What is Hund's principle of maximum multiplicity; Pauli's exclusion principle?
20. Show the placement of electrons in orbitals for each of the following: Ca, Y, Rn, element 104.
21. Explain how the long form of the periodic table is of help in keeping track of the order of filling various sublevels.
22. What is probably the number of sublevels in the fifth main energy level; the number of orbitals; the maximum number of electrons? Is an element known whose atoms have this maximum number of electrons in the fifth level? What would be a likely atomic number of the element? What assumptions have you made in arriving at this number?
23. Beginning with sodium in period 3, the first ionization energies increase regularly to the end of the period except that of aluminum is less than that of magnesium and that of sulfur is less than phosphorus. In terms of atomic structure, why should the ionization energy increase from left to right through a period? How can the smaller values of aluminum and sulfur be accounted for in terms of orbital theory?
24. Does the statement "an s orbital has a spherical shape" contradict the uncertainty principle? Explain.
25. Describe some of the difficulties encountered when one attempts to describe photons and electrons with words.

### **SUPPLEMENTARY READING**

- 
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**ELECTRONIC STRUCTURE  
OF ATOMS**

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# CHEMICAL

## CHANGES AND CHEMICAL

### BONDS



#### EVIDENCE FOR CHEMICAL CHANGES

A substance, sometimes called a pure substance for emphasis, is a kind of matter that is characterized by a unique set of physical and chemical properties. A substance may break down into simpler substances, or it may join with another substance only by chemical reaction. We recognize two classes of substances: **elements** and **compounds**. An element is a substance made of one type of atom, whereas a compound is made of two or more types of atoms joined in a definite ratio.

According to atomic theory, in elements except noble gases or in compounds atoms are held together by strong forces of attraction called chemical bonds. During chemical reactions one or both of the following take place: bonds in the original substances are broken; bonds holding the atoms of the new substances together are formed.

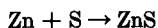
Because atoms cannot be observed, how does one know when substances undergo chemical reaction? Generally, there are three types of experimental observations that indicate the occurrence of chemical changes. The substances involved are observed carefully to determine if there is a *change in their properties*, or a *change in composition*, or a *change in energy* at the time of a suspected reaction.

#### PROPERTIES AND CHEMICAL CHANGE

One indication of a chemical change is the observation of changes in the properties of matter. Let us take two substances from the shelf in the kitchen: vinegar and soda. These are the *reactants*. If we sprinkle a little soda in the vinegar, several obvious changes take

place. A great many bubbles of gas are given off; the solution that results may taste like neither vinegar nor soda; and if we evaporate the solution to dryness, the white solid remaining is quite different from the original soda. The properties of the resulting white solid and of the gas given off are unlike the properties of either the vinegar or the soda. The solid and the gas are the *products* of a chemical reaction.

Consider finely powdered sulfur mixed with zinc filings. When these reactants are heated, a violent change takes place, and a third substance, the product, is formed; it resembles neither zinc nor sulfur. Sulfur melts at  $114^{\circ}\text{C}$ , and zinc melts at  $420^{\circ}\text{C}$ , but the product vaporizes without melting (*sublimes*) at  $1180^{\circ}\text{C}$ . Sulfur dissolves in a liquid called carbon disulfide, but the new substance does not. Zinc can be bent and formed into various shapes, but the new substance is brittle and cannot be bent without breaking. In short, the substance formed when sulfur is heated with zinc is the compound zinc sulfide, which has its own properties:



*If two substances are brought together (synthesis) or if one substance is broken down (decomposition) and products are formed that have properties different from those of the original substances, a chemical reaction has taken place.*

## COMPOSITION AND CHEMICAL CHANGE

As described in Chap. 1, a pure compound is always composed of certain elements combined in a definite proportion by weight (the law of definite composition). The fact that a compound has a certain, reproducible composition is useful in determining when a chemical change takes place.

When pure oxygen gas is passed over powdered iron heated to just below  $500^{\circ}\text{C}$ , a substance is produced that has the composition 72.36 per cent iron and 27.64 per cent oxygen. At a higher temperature, say above  $600^{\circ}\text{C}$ , continued passing of oxygen results in the formation of a second substance that is 69.94 per cent iron and 30.06 per cent oxygen. If the supply of oxygen is then limited and the second substance is heated for a long time above  $600^{\circ}\text{C}$ , still a third substance is formed that is 77.73 per cent iron and 22.27 per cent oxygen. Although the second substance is usually reddish, each of these three oxides of iron can be black, so that they may not be easily distinguished. However, because of the reproducible, definite compositions of these substances, it is obvious that different chemical reactions occur under conditions of different temperature and amount of oxygen present. The formulas of the three compounds are  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{FeO}$ , respectively.

*If two or more substances are brought together or if a single substance*

*breaks down and a new substance is formed which has a definite composition of its own, a chemical reaction has taken place.*

*Isotopes and Limitations of Law of Definite Composition.*

Prior to the discovery of isotopes, a compound was believed to be composed of two or more elements united always in the same proportion by weight (law of definite composition). An example will show certain limitations of this law. Water as it occurs in nature has a composition of 88.81 per cent oxygen and 11.19 per cent hydrogen. However, water can actually have a range of composition, depending on which isotope of hydrogen is united to which isotope of oxygen. For example, it is possible to have water that is made up solely of hydrogen atoms of weight 1 united with oxygen atoms of weight 16 or to have water made up of hydrogen atoms of weight 2 united with atoms of oxygen with weight 16. Several possible percentage compositions are shown in the following tabulation. The mass numbers of hydrogen and oxygen atoms are indicated by superscript numbers. (See Table 2-1 for weights of these isotopes.)

	percentage of hydrogen by weight	percentage of oxygen by weight
$^1\text{H}_2^{16}\text{O}$	11.11	88.89
$^2\text{H}_2^{16}\text{O}$	20.12	79.88
$^1\text{H}_2^{17}\text{O}$	10.52	89.48
$^2\text{H}_2^{17}\text{O}$	19.05	80.95

We see, then, that compounds may not always have their elements combined in a definite proportion by weight, although the proportion of atoms in a molecule is definite. In the case of water the atomic ratio is always two atoms of hydrogen to one atom of oxygen.

*Definite Composition in Nature.* It is common to find the various isotopes of an element so uniformly mixed in nature that any sample of the element will be composed of atoms whose average weight is the atomic weight listed in the table of the elements (inside the front cover). Unless the isotopes have been separated, we shall find that compounds do have a definite composition by weight. In the three oxides of iron previously described, the iron-oxygen ratio of atoms is either 3:4 or 2:3 or 1:1. By using isotopes, many differing weight compositions could be attained, but in nature the average weights of iron and oxygen atoms are 55.85 and 15.999. The three compounds, therefore, have definite compositions, whether found in nature or made from iron and oxygen prepared from natural sources.

## ENERGY AND CHEMICAL CHANGE

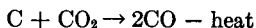
We shall refer to the examples cited above in order to illustrate a general rule of great importance. When vinegar and soda react chemically, the substances that result are slightly warmer than the

## CHEMICAL CHANGES AND CHEMICAL BONDS

original substances. In the case of powdered zinc and sulfur, when the chemical reaction takes place, so much energy is liberated that a violent explosion takes place, and heat and light are emitted. The fact that this reaction gives off heat is shown in a chemical equation as follows:



Conversely, some reactions do not give off heat but require it. The reaction of carbon dioxide with carbon to form carbon monoxide proceeds readily only at a high temperature, and this reaction continues to take place only if heat is continually applied. In equation form this is shown by a negative heat term on the right:



Every chemical reaction involves a change in energy.<sup>1</sup> Either the reaction takes place and energy is liberated to the adjacent surroundings, or the reaction takes place and energy is absorbed from the adjacent surroundings. As pointed out in Chap. 1, the first type of reaction is called exothermic (heat comes out), and the second endothermic (heat goes in). All chemical reactions are in one of these two classes. Both classes are considered from the standpoint of the heat contents of reactants and products in Chap. 5.

Because an endothermic reaction absorbs heat from its surroundings, heat must be continually available or the reaction will become slower and slower, till the rate of reaction drops practically to zero. On the other hand, many exothermic reactions proceed more and more rapidly as long as reactants are available in large enough amounts. If the heat evolved during the reaction of some of the reactants serves to increase the energy of neighboring reactants sufficiently, these neighboring substances will react and evolve more heat, and so on. The burning of any common fuel is an example of an exothermic reaction that tends to go on as long as there are reactants (fuel and oxygen) available. Of course, if too much of the heat from the reaction is dissipated to nonreactive materials or to the surroundings, the temperature drops and the burning ceases.

*If substances are brought together or if a single substance breaks down and the process is either endothermic or exothermic, a chemical reaction may have taken place.* Because energy changes also occur in physical processes, however, a change in energy is not conclusive evidence that a chemical change has occurred.

### SUMMARY

There are three main kinds of evidence that the chemist uses to determine whether substances react chemically when they are brought together. Chemical bonds are evidently made or broken when (1)

<sup>1</sup> For some reactions a temperature can be calculated at which the change in heat energy would be zero. However, it would be quite unusual for the reaction to be taking place at precisely that temperature.

the properties of the substances change, (2) substances of different composition are formed, and (3) there is a change in energy due to the interaction of the substances.

## HOW ATOMS COMBINE

Since the discovery of the electronic structure of atoms, chemists and physicists have been able to investigate the ways in which atoms of one kind join with another. The guiding principle, developed today in great detail, is that atoms act on one another by way of their outer electrons. This interaction of electrons leads to the strong forces of attraction, chemical bonds, that hold atoms together in compounds.

A compound has no resemblance to the elements from which it is formed; it must be considered a unique substance in its own right. The characteristics of a compound depend in great measure on the types of chemical bonds that hold its atoms together. In this chapter we begin the study of the various types of chemical bonds that enable a little more than 100 different atoms to combine to form more than 1 million compounds.

When a piece of iron rusts in air—the reactants are Fe, O<sub>2</sub>, H<sub>2</sub>O, and CO<sub>2</sub>—one of the products of the reaction is apparently a hydrated oxide of iron, that is, Fe<sub>2</sub>O<sub>3</sub> combined with H<sub>2</sub>O molecules. We seek to understand this and other chemical changes by focusing our attention on the individual particles of the elements that are involved—the atoms.

**Valence.** From the formulas of compounds, it is clear that different atoms have different powers of combining with each other. As Dalton's atomic theory was developed, formulas, such as H<sub>2</sub>O, HCl, CaCl<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, CO, FeO, Fe<sub>2</sub>O<sub>3</sub>, NH<sub>3</sub>, were assigned to compounds on the basis of percentage compositions and atomic weights. The combining capacity or **valence** of an element was defined as the number of atoms of hydrogen that one atom of an element could combine with or take the place of in forming compounds. As indicated by the formulas, in H<sub>2</sub>O, oxygen has a valence of 2; in HCl, chlorine has a valence of 1; and in NH<sub>3</sub> and CH<sub>4</sub>, nitrogen and carbon have valences of 3 and 4, respectively. In CaCl<sub>2</sub>, calcium takes the place of two hydrogens, so that it is assigned a valence of 2; in CO<sub>2</sub>, carbon is given a valence of 4, but in CO, its valence is 2; iron has a valence of 2 in FeO but 3 in Fe<sub>2</sub>O<sub>3</sub>. Today, with the development of later ideas about chemical reactions based on the electronic structures of atoms, the early definition of valence is of little value. But the word valence is often used to refer to the combining power of an atom, and valence numbers are still assigned on the basis of formulas of compounds.

**Atomic Structure and Chemical Reactions.** The most important structural feature of atoms in determining chemical behavior is the number of electrons in their outermost energy levels. When atoms of one element combine with those of another, there is always some change in the distribution of electrons in the outermost energy levels. The study of many elements and compounds has led to the idea that, in compound formation, atoms of certain elements tend to gain electrons, and others tend to lose. As a result of these tendencies, two atoms may *transfer* or *share* electrons, and either process may provide for a stable arrangement of electrons between the atoms that results in the formation of a compound. The electrons that are involved in a chemical reaction are called the *valence electrons* of an atom.

The elements are roughly divided into four classes. Elements whose atoms usually lose electrons in compound formation are *metals*; those whose atoms often gain electrons are *nonmetals*. A class between these is called the *metalloids*, or *borderline elements*. The fourth class consists of the *noble gases*, six elements that do not combine with other substances readily. No compounds of the lighter noble gases are known, and only a few compounds have been prepared of the heavier ones, notably xenon.

These four classes of elements are indicated in the periodic table inside the front cover. The heavy vertical line at the far right of the table marks off the six noble gases in group VIIIA. In the middle of the right-hand page there is a heavy zigzag line that separates the metals (to the left) from the nonmetals (to the right). This division is not at all sharp. Near this line are the metalloids, such as germanium, Ge, arsenic, As, and antimony, Sb.

## INFERENCES FROM PROPERTIES OF NOBLE GASES

The mere fact that there is a family of elements whose members form compounds rarely, if at all, indicates that atoms of these elements have very stable electron arrangements. Evidently atoms of the noble gases have little tendency to gain, lose, or share electrons with other atoms; their electron levels are of relatively low energy. Prior to 1962, the elements in group VIIIA were called *inert*, because they were thought to be completely unreactive. In that year the first compounds were made, an interesting episode in chemistry that is discussed in Chap. 29.

The arrangement of electrons in the noble gases is summarized in Table 4-1. The table shows that, except in the first main level, there can be no more than eight electrons in any level when it is the outer one. In Table 3-3 the electron arrangement of neon is given as



Arrangement of electrons in noble gases

TABLE 4-1

noble gas	symbol	atomic number	number of electrons by main energy levels*					
			1	2	3	4	5	6
helium	He	2	2					
neon	Ne	10	2	8				
argon	Ar	18	2	8	8			
krypton	Kr	36	2	8	18	8		
xenon	Xe	54	2	8	18	18	8	
radon	Rn	86	2	8	18	32	18	8

\* The numbers 1 to 6 are the principal quantum numbers that denote the different main levels. See Table 3-2.

For each of the larger noble-gas atoms a similar outer electron structure is formed in which a *p* sublevel is completed. The eight electrons in the outer main level of an argon atom are designated as  $3s^23p^6$ , in krypton as  $4s^24p^6$ , in xenon as  $5s^25p^6$ , and in radon as  $6s^26p^6$ .

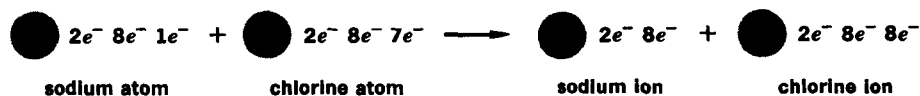
The arrangement of electrons in these six atoms that do not combine or rarely combine chemically with others gives us a clue to how atoms interact with one another in general. It is thought that, by combining with one another, atoms of many of the other elements tend to achieve electron stability comparable with that of the noble gases. Such stability is attained in one of two ways: (1) by the *transfer* of outer-shell electrons from the atoms of one element to those of another, or (2) by the *sharing* of electrons by two or more atoms.

The new substances that result when two or more elements combine by sharing or transferring electrons are called **compounds**.

## TRANSFER OF ELECTRONS

*In general, when a metallic element combines with a nonmetallic element, electrons are lost by atoms of the metal and gained by atoms of the nonmetal.*

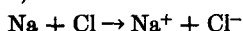
Atoms of lithium, sodium, and potassium lose one electron easily; beryllium, magnesium, and calcium lose two. These six elements are metals. Fluorine and chlorine atoms each gain one electron; oxygen and sulfur atoms each gain two. These four elements are nonmetals. When a sodium atom loses an electron to a chlorine atom, we say that they have *combined* to make sodium chloride, NaCl (ordinary



Sodium and chlorine atoms react by the transfer of an electron to yield ions.

FIG. 4-1

table salt). The reaction between the sodium and chlorine atoms can be indicated as in Fig. 4-1, or it can be written thus:





## CHEMICAL CHANGES AND CHEMICAL BONDS

The above representation of this reaction is called a **chemical equation**. In an equation all the substances are represented by symbols, the reactants being shown on the left of the arrow and the products on the right.

The symbol Na refers to the sodium atom, which has a net charge of zero; the symbol  $\text{Na}^+$  refers to the sodium *ion*, which has a net charge of  $1+$  ( $11p$  in the nucleus,  $10e^-$  outside). The symbol  $\text{Cl}^-$  refers to an *ion* of chlorine, which has a net charge of  $1-$ .

When electrons are transferred from one atom to another, ions are formed. Some of the ions will be positive, others negative. Let us show how magnesium atoms combine with fluorine atoms. Magnesium tends to lose two electrons and have an outside shell with eight

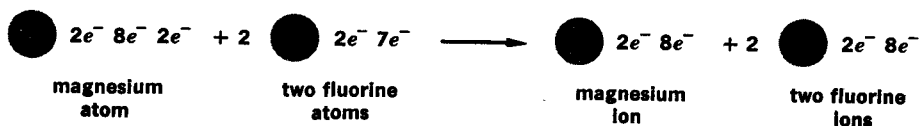
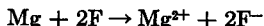


FIG. 4-2 A magnesium atom gives up two electrons to form a stable  $\text{Mg}^{2+}$  ion; a fluorine atom gains one electron to form a stable  $\text{F}^-$  ion. Hence, magnesium and fluorine react in a 1:2 ratio by atoms.

electrons (Fig. 4-2). Fluorine tends to gain one electron in order to complete its outside shell:



The magnesium atom loses two electrons to form a magnesium ion with a charge of  $2+$ . The particle formed when the fluorine atom gains one electron is an ion of fluorine, which has a charge of  $1-$ . The formation of *one* magnesium ion must result in the formation of *two* ions of fluorine.

**Electronic Structure of Ions.** The remarkable stability of an outside shell that has eight electrons is evident not only in the noble-gas atoms but in ions of other atoms. Thus magnesium (atomic number 12) forms a dipositive ion, whereas chlorine (atomic number 17) forms a uninegative ion. The arrangement of electrons of these atoms and ions is as follows:

atoms				ions			
Mg	$2e^-$	$8e^-$	$2e^-$	$\text{Mg}^{2+}$	$2e^-$	$8e^-$	
Cl	$2e^-$	$8e^-$	$7e^-$	$\text{Cl}^-$	$2e^-$	$8e^-$	$8e^-$

The magnesium ion has an electronic structure similar to that of the neon atom,  $1s^2 2s^2 2p^6$ ; the chloride ion is electronically similar to the argon atom,  $1s^2 2s^2 2p^6 3s^2 3p^6$ . There is a tendency for atoms with atomic numbers within about three units of that of a noble gas to gain or lose electrons so as to form ions with "noble-gas structures" having eight electrons outside. This tendency was called the *rule of*

eight<sup>1</sup> long before it was correlated with the  $s^2p^6$  structures in the outside main energy level.

We can often predict the electronic structure of ions from the structure of their atoms. Using the scheme introduced in Chap. 3, the structure for an yttrium atom, number 39, is written as  $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^1$ . We would predict that yttrium would lose three electrons to form a  $Y^{3+}$  ion, having a structure similar to krypton:  $1s^22s^22p^63s^23p^64s^23d^{10}4p^6$ . The structure of an arsenic atom is written as  $1s^22s^22p^63s^23p^64s^23d^{10}4p^3$ . We would predict that arsenic would gain three electrons to form  $As^{3-}$ . The completion of the  $p$  sublevel would be shown by writing  $4p^6$  for the last term, indicating that  $As^{3-}$  has a structure similar to krypton. The  $As^{3-}$  and the  $Y^{3+}$  ions have similar electronic structures.

As a rule, electrons in the outer main energy level are lost first in forming ions, although in the theoretical build-up of the atom they may not be the last electrons added. Gallium atoms commonly lose three electrons to form  $Ga^{3+}$  ions. The atom has the structure  $1s^22s^22p^63s^23p^64s^23d^{10}4p^1$ . The ion has a similar structure, but without the  $4s^2$  and  $4p^1$  electrons. The  $4s^2$  electrons are lost and the  $3d^{10}$  electrons remain, although the  $d$  electrons were added later in the theoretical build-up of the atom. Iron is another good example of this general rule. It is known to form ions by the loss of either two or three electrons. Iron atoms have a complete structure of  $1s^22s^22p^63s^23p^64s^23d^6$ . Looking at only the outer two sublevels, we can write



When iron forms an  $Fe^{2+}$  ion, it is believed to lose its two  $4s$  electrons. When iron forms an  $Fe^{3+}$  ion, it loses two  $4s$  electrons and one of the electrons from the only filled  $3d$  orbital. Each of the  $3d$  orbitals in  $Fe^{3+}$  then has a single electron; to remove one of these electrons requires so much energy that  $Fe^{4+}$  is not formed in ordinary chemical reactions.

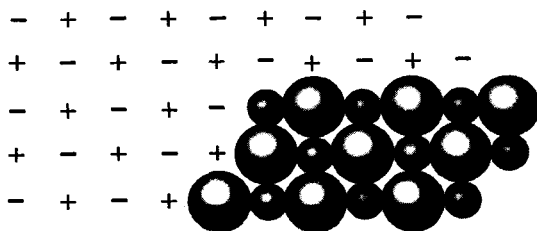
It might seem reasonable that the last electrons added would be in the highest energy levels and therefore lost most easily. However, the loss of electrons to form ions is not simply the reverse of the imaginary build-up of an atom according to its position in the periodic table. In the build-up scheme, we consider the addition of a proton and an electron for each new atom; but in forming ions, electrons only are lost, and the positive charge on the nucleus remains the same. The electrons with the highest principal quantum number, that is, those in the outer main level, are usually lost first in forming an ion.

<sup>1</sup> Elements with atomic numbers 1, 3, 4, and 5 tend to follow a rule of two and to form ions with electronic structures similar to helium, that is, a single energy level designated  $1s^2$ .

## CHEMICAL CHANGES AND CHEMICAL BONDS

**Limitation of Rule of Eight.** The idea that ions are formed when atoms gain or lose electrons to attain the structure of a noble gas is a rule that is sometimes of value, sometimes not. In the examples that we have given in this chapter, the rule of eight enables us to predict the ionic structures of  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{F}^-$ ,  $\text{Y}^{3+}$ , and  $\text{As}^{3-}$  correctly. But the structures of  $\text{As}^{3+}$ ,  $\text{As}^{5+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$  are not similar to any of the noble gases, so that the rule of eight is of no use in these cases. In beginning our study of ions we shall limit our predictions to those ions which do achieve a structure with eight electrons in their outer main levels. However, we shall also encounter examples of other types of ions formed by many common elements, such as the ions of iron and arsenic just mentioned. We shall memorize these ionic charges as we need them; as we develop more skill in using sublevel structures, we shall be able to predict charges on some ions that do not follow the simple rule of eight.

**Ions Differ from Atoms.** When the atoms of two elements combine with each other by transferring electrons, the substance formed does not resemble either of the original materials. The new substance is composed, not of atoms, but of ions. These ions, some positive, some negative, are strongly attracted to one another by the electrostatic attraction that exists between unlike charges. The modern theory regarding the structure of a substance such as sodium chloride is that it consists of positive and negative ions arranged in well-ordered fashion in a crystal. Each positive ion is surrounded by negative ions, each negative ion by positive ones, as shown in Fig. 4-3. The attraction that binds unlike ions together is termed an



A diagram showing one layer of particles in one type of ionic crystal. In three dimensions each positive ion will have six negative ions as its closest neighbors.

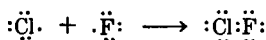
FIG. 4-3

**electrovalent bond.** Both sodium chloride and magnesium fluoride are called **electrovalent compounds**. Their chemical formulas are written  $\text{NaCl}$  and  $\text{MgF}_2$ , respectively.

## SHARING OF ELECTRONS

Two atoms, both of which tend to gain electrons, may combine with each other by sharing one or more pairs of electrons. For example, an atom of fluorine and an atom of chlorine, each having seven electrons in its outer shell, unite by sharing two of these fourteen elec-

trons between them. This is shown diagrammatically as follows, using dots to indicate only the electrons in the outside main levels:



As a result of sharing a pair of electrons, each atom has a complete shell of eight electrons. By "complete" is meant an outside shell similar to a noble gas. For many simple compounds, the rule of eight is a satisfactory guide for predicting the number of electrons to be shared in building up the outside shell of electrons.

The strong force that binds the chlorine atom to the fluorine is the attraction of each for the electrons that are held jointly. A shared pair of electrons is called a **covalent bond**. Compounds whose atoms are joined by covalent bonds are called **covalent compounds**.

The *single particle* formed by the union of one chlorine atom with one fluorine atom is uncharged, because it contains the same number of protons as it does electrons, namely, 26 of each. An uncharged particle resulting from the union of two or more atoms is called a **molecule**.<sup>1</sup> The molecule ClF is the smallest particle of chlorine fluoride. A cubic centimeter sample of it contains many millions of molecules.

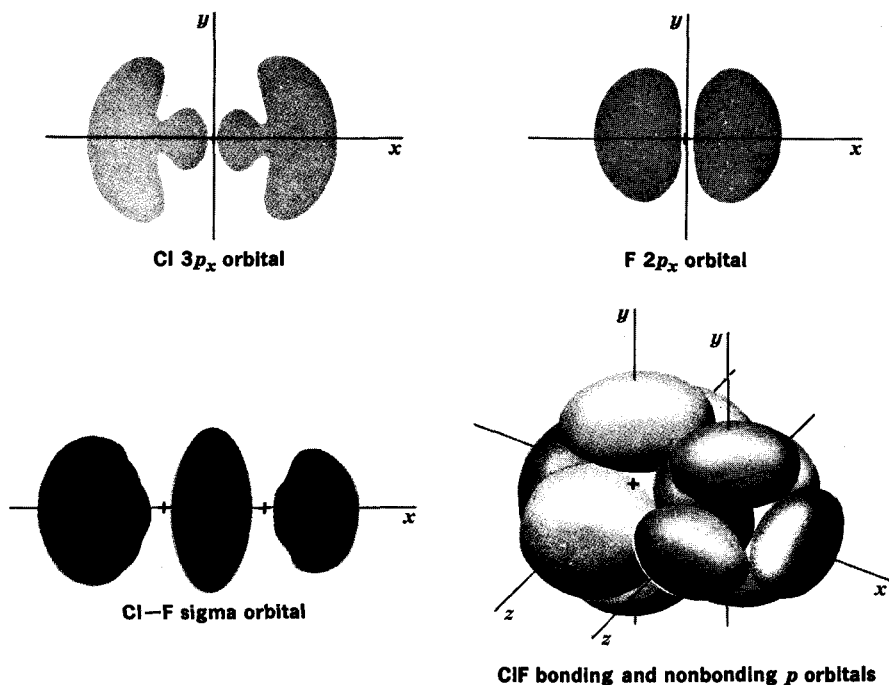
**Molecular Orbitals.** The structure of a chlorine atom is  $1s^2 2s^2 2p^6 3s^2 3p^5$ , and that of a fluorine atom is  $1s^2 2s^2 2p^5$ . One way of picturing the formation of the covalent bond between these two atoms is to consider the interaction of the two electrons in the partially filled *p* orbitals, as shown in Fig. 4-4. The probable regions of space occupied by the shared electrons is called a *molecular orbital*.<sup>2</sup> A molecular orbital is not simply two overlapping atomic orbitals; the molecular orbital has a shape all its own that is determined by the types of atomic orbitals used and by the particular atoms being held. If a molecular orbital is symmetrically arranged around the line passing through two nuclei, it is called a **sigma orbital** or *sigma bond*. The interaction of two *p* orbitals can lead to a sigma bond, as shown in Fig. 4-4. A line drawn through the centers of the two atoms joined by a sigma bond is arbitrarily called the *x* coordinate, and the two atomic *p* orbitals that form the bond are therefore designated as the  $p_x$  orbitals. (Compare Fig. 3-11.)

The hydrogen atom is noted for its tendency to form covalent bonds. The sharing of electrons between H $\cdot$  and  $\cdot\ddot{\text{Cl}}:$  leads to the

<sup>1</sup> The term molecule refers to the smallest particle of a nonionic substance that has the characteristics of the substance. In the case of a compound the molecule must consist of two or more atoms, but in the case of elements the single atoms may be characteristic of a quantity of the element. (See section on Individual Particles in Gases, Chap. 7.)

<sup>2</sup> The term molecular orbital as used in this text simply refers to a bonding orbital in a covalent compound. The student is referred to advanced texts for specific descriptions of the valence bond (VB) or molecular orbital (MO) theories, and other theories of chemical bonding.

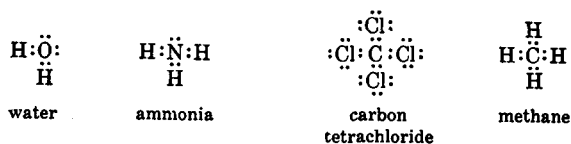
**CHEMICAL CHANGES AND  
CHEMICAL BONDS**



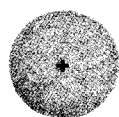
**FIG. 4-4** The overlap along the  $x$  axis of two unfilled  $p$  orbitals forms the sigma bond in the covalent compound chlorine fluoride, ClF.

formation of  $\text{H}:\text{Cl}:$ , a covalent molecule. The outside energy level of hydrogen is filled when it contains two electrons (similar to helium,  $1s^2$ ). In Fig. 4-5 the sigma bond in HCl, formed by the interaction of the  $1s$  orbital of hydrogen with the  $3p_x$  orbital of chlorine, is diagrammed.

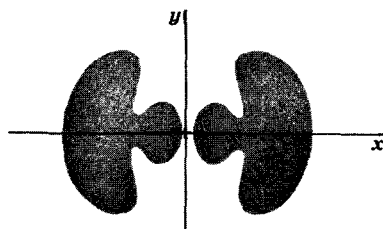
The hydrogen atom and the carbon atom are well known for their tendencies to form covalent bonds with other atoms. The electron-dot formulas for water ( $\text{H}_2\text{O}$ ), ammonia ( $\text{NH}_3$ ), carbon tetrachloride ( $\text{CCl}_4$ ), and methane ( $\text{CH}_4$ ) can be written on the basis of the rule of eight (rule of two for hydrogen):



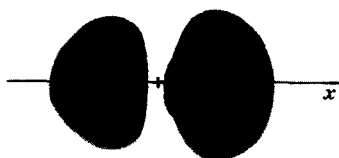
It is also common, in indicating the structure of molecules, to use a dash for a pair of shared electrons when only the electrons that are shared are indicated.



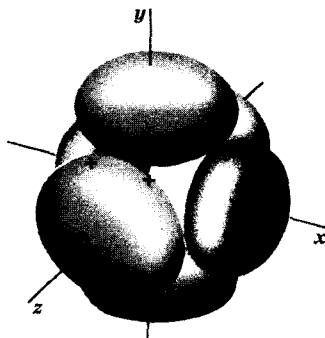
H 1s orbital



Cl  $3p_x$  orbital



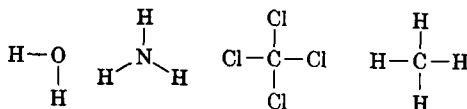
HCl sigma orbital



HCl bonding and nonbonding orbitals

FIG. 4-5

Bonding orbital in HCl molecule. The sigma bond is formed by the interpenetration of the 1s orbital of hydrogen and the  $3p_x$  orbital of chlorine.



The molecular orbitals in these molecules can be diagrammed by considering the atomic orbitals available for bonding and by using information about molecular structure that has been arrived at by X-ray studies and other methods. The angle between the two H—O bonds in water is known to be about  $104^\circ$ ; the angle between two H—N bonds in ammonia is  $107^\circ$ ; and the angle between Cl—C bonds or H—C bonds in the two carbon compounds is  $109^\circ 28'$ , the well-known tetrahedral angle. The diagrams in Fig. 4-6 are drawn on the basis of these data. Each of the four molecules has some relation to the regular four-sided figure, the tetrahedron.  $\text{CH}_4$  and  $\text{CCl}_4$  have perfect tetrahedral symmetry so far as is known.  $\text{NH}_3$  has its three hydrogens directed almost toward three corners of an imaginary tetrahedron and its pair of nonbonding electrons toward the fourth corner. In  $\text{H}_2\text{O}$ , the two hydrogens are directed roughly toward two corners of a tetrahedron and the two nonbonding orbitals toward the other two.

## CHEMICAL CHANGES AND CHEMICAL BONDS

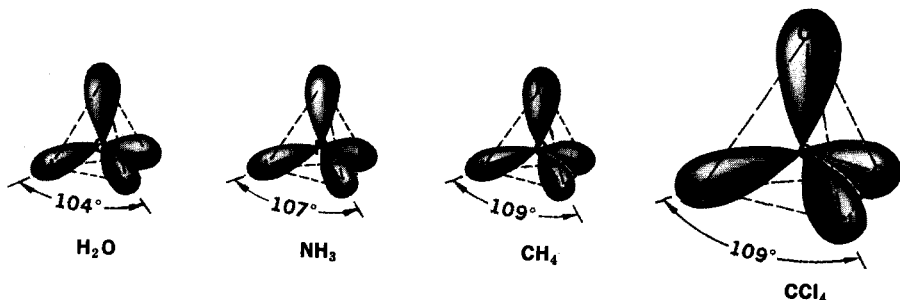


FIG. 4-6 Diagrams showing unshared electron pairs (gray), sigma bonds, and bond angles in molecules of water, ammonia, carbon tetrachloride, and methane.

The use of models also helps us visualize molecular structure. In Fig. 4-7 diagrams of models of the four molecules that we have been discussing are shown. In such models as these, the nonbonding orbitals are not indicated.

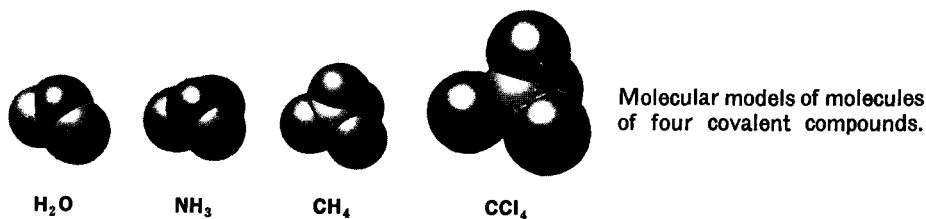
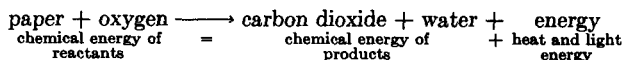


FIG. 4-7

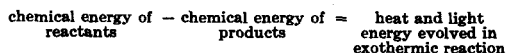
**OTHER TYPES OF MOLECULAR ORBITALS.** The sigma orbital is the simplest type of molecular orbital. Later we shall discuss the pi ( $\pi$ ) type of orbital, which arises from the interaction of  $p$  orbitals that are not directed along the line joining the centers of the two bonded atoms.

**Atomic Theory and Chemical Energy.** All changes in the position or in the properties of matter involve changes in energy. Water gives up energy as it flows from a higher elevation toward the sea; a piece of iron takes up energy as its temperature increases; and energy is given up during the chemical change of the burning of paper in oxygen to yield carbon dioxide and water.

In the case of the falling water, we speak of potential energy being changed to kinetic energy and heat energy (see Fig. 1-1); in the case of the iron, we think of the iron atoms becoming more highly excited as they absorb energy and increase in temperature; and for the combustion of paper, we say that the carbon dioxide and water produced have less chemical energy than the original paper and oxygen. In this chemical reaction, some chemical energy is changed to heat and light energy.



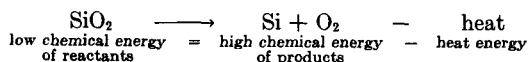
or



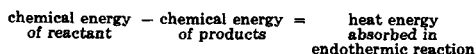
Atomic theory, with its postulates of chemical bonds between atoms, suggests a way of accounting for the fact that some chemical reactions evolve energy whereas others absorb it. In chemical reactions it is assumed that atoms interact with one another by means of their outermost electrons. When elements and compounds react, there is always some change in the arrangements of the atoms themselves and in the arrangements of the electrons in the outermost energy levels of the atoms involved. As electrons are transferred or shared in new ways, some chemical bonds are broken and new ones are made.

Every chemical bond, ionic or covalent, has a certain bond energy associated with it. The **bond energy** is the amount of energy given up when a bond is formed; this same amount of energy is taken up when this bond is broken. In a complex reaction, such as the burning of paper, many bonds in the reactants are broken and other types of bonds are formed in the products. If the total energy necessary to break the bonds in the reactants is less than the energy given up in forming the bonds in the products, the reaction is exothermic. If the total bond energies in the reactants is more than in the products, the reaction is endothermic.

A substance that is held together by very strong bonds usually has a relatively low chemical energy. When such a substance is decomposed into its elements, the reaction is endothermic. Consider the decomposition of silica,  $\text{SiO}_2$ :



or



**Hybridized Orbitals.** As pointed out previously, the shape and direction of a molecular orbital differ from the atomic orbitals that form it. The case of carbon and its compounds is of great importance, for carbon forms such a wide variety of compounds. In an isolated carbon atom, the most stable state is thought to be that in which two of the four outside electrons occupy the  $2s$  orbital as paired electrons and each of the remaining two occupies separate  $2p$  orbitals, that is,  $1s^2 2s^2 2p^2$ . On the basis of this atomic orbital structure and assuming the use of only the two  $p$  orbitals, we might predict that a carbon atom would react with two hydrogen atoms to form  $\text{CH}_2$  and that the two C—H bonds would be at right angles. However, it is



## CHEMICAL CHANGES AND CHEMICAL BONDS

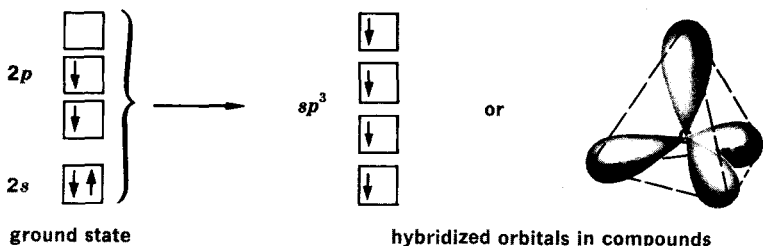


FIG. 4-8

A schematic representation of the four  $sp^3$  bonding orbitals of a carbon atom.

found experimentally that a carbon atom reacts with four hydrogen atoms to form  $\text{CH}_4$  and that the molecule has the symmetrical shape indicated in Fig. 4-6. Because the molecule is symmetrical, the four bonds are assumed to be alike.

To account for the formation of four identical C—H bonds, we assume that all four valence electrons of carbon participate in bond formation. Although the elevation of one of the  $2s$  electrons into a vacant higher-energy  $2p$  orbital would increase the energy of the isolated atom, this condition would provide four separate orbitals (one  $2s$  and three  $2p$ ) with four unpaired electrons. Such an atom could then form four energy-lowering bonds with other atoms to produce a stable molecule (see Fig. 4-8). The energy required to elevate the  $s$  electron (an endothermic process) is more than compensated for by the energy given off in the formation of more bonds with hydrogen (an exothermic process).

Carbon, of course, does form four covalent bonds with other atoms. A striking characteristic of these bonds in the simplest carbon compounds is their equivalence. For example, the four carbon-hydrogen bonds in methane are identical in stability and reactivity. To account for the four identical bonds, we assume that the elevation of a  $2s$  electron to a  $2p$  orbital is accompanied by an interaction or **hybridization** of the four resulting orbitals to form orbitals that are identical in all respects. Because these hybrid orbitals result from the blending of one  $s$  and three  $p$  orbitals, they are referred to as  $sp^3$  (pronounced s-p-three) orbitals.

The most important characteristics of the carbon  $sp^3$  orbitals are:

1. There are four such orbitals.
2. They are identical.
3. They are directed in space from a carbon nucleus at the center toward the four corners of an imaginary tetrahedron.

The hybridization of orbitals is also characteristic of atoms of other elements. For example, in boron atoms containing two  $2s$  and one  $2p$  electrons, a  $2s$  electron during compound formation is elevated to a vacant  $2p$  orbital with the resultant hybridization of the three orbitals ( $sp^2$  orbitals). In boron trichloride ( $\text{BCl}_3$ ), the B—Cl bonds

are identical, and all atoms are in a single plane, the bond angles being  $120^\circ$ .

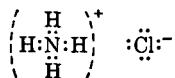
**Lewis Electron-dot Formulas.** In describing the sharing of electrons, we have, in several places, used formulas in which outer-level electrons are represented simply as dots around symbols, for example,  $\cdot\ddot{\text{Cl}}:\ddot{\text{F}}\cdot$  for chlorine fluoride. Such formulas are called Lewis formulas, in honor of G. N. Lewis, who, in 1916, proposed that a covalent bond consisted of a pair of shared electrons and that four pairs of electrons constituted a stable outside shell that atoms tended to achieve in compound formation. Modern orbital theories have outdated these simpler formulas, but for many purposes they are still valuable and are often used to account for the combining ratios in compounds.

Lewis formulas can also be used to represent ionic compounds. Magnesium chloride,  $\text{MgCl}_2$ , can be written  $\text{Mg}^{2+}$ ,  $\cdot\ddot{\text{Cl}}:^-$ ,  $:\ddot{\text{Cl}}:^-$ , the commas indicating that the ions are separate particles formed by the transfer of electrons rather than sharing. Because the two outer electrons of the magnesium ion have been lost in forming the ion, they are not shown. Alternatively, the magnesium ion can be written  $:\ddot{\text{Mg}}^{2+}$ ; with no electrons in the third main level, the ion now has an outer level of eight electrons in the second main level (see Fig. 4-2). Potassium oxide,  $\text{K}_2\text{O}$ , is written as  $\text{K}^+$ ,  $\text{K}^+$ ,  $:\ddot{\text{O}}:^{2-}$  or as  $:\ddot{\text{K}}:^+$ ,  $:\ddot{\text{K}}:^+$ ,  $:\ddot{\text{O}}:^{2-}$ .

## ELECTROVALENT AND COVALENT BONDS

It is a great temptation to try to classify things according to hard and fast rules. We must beware of generalizing too quickly and too definitely in our study of chemistry. Although electrovalent compounds and covalent compounds are the two principal types of chemical substances, there are many compounds that do not fit well into either class.

**Polyatomic Ions.** There are compounds that are held together by both electrovalent and covalent bonds. In the compound ammonium chloride,  $\text{NH}_4\text{Cl}$ , the four hydrogens are held to the nitrogen by covalent bonds to form the ion particle  $\text{NH}_4^+$ . This positive ammonium ion is attracted as a unit to neighboring  $\text{Cl}^-$  ions. The attraction of such unlike charges constitutes an electrovalent bond between these ions. The charges on the ions are made clear by the following formulas, which indicate the number of outer electrons:

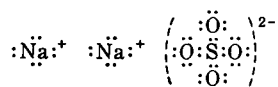


A nitrogen atom has 5 outer electrons; a hydrogen atom has 1. One nitrogen plus 4 hydrogens involves 9 outer electrons; because

## CHEMICAL CHANGES AND CHEMICAL BONDS

there are only 8 in the  $\text{NH}_4^+$  particle, this ion has a net charge of  $1+$ . The electron missing from the  $\text{NH}_4^+$  ion is held by the chlorine in its complete outer level (forming a  $\text{Cl}^-$  ion).

Another example is sodium sulfate,  $\text{Na}_2\text{SO}_4$ . A sodium ion,  $\text{Na}^+$ , results when a sodium atom loses 1 electron (the outer level of the ion then has 8 electrons). For 1 sulfur atom (6 outer electrons) and 4 oxygen atoms (24 outer electrons), there are a total of 30 outer electrons. But the  $\text{SO}_4^{2-}$  ion, as indicated by the dot formula, includes 32 outer electrons:



This excess of 2 electrons is in agreement with its charge of  $2-$ . This 2-electron excess also accounts for the electrons lost by 2 sodium atoms in forming ions.

Compounds such as  $\text{NH}_4\text{Cl}$  and  $\text{Na}_2\text{SO}_4$  are classed as electrovalent compounds, because they contain ions held together by electrovalent bonds. However, within the  $\text{NH}_4^+$  ion and the  $\text{SO}_4^{2-}$  ion there are covalent bonds between the various parts. These covalent bonds are sufficiently strong so that the whole ion acts in many ways as a unit particle. Thus ammonium ions and sulfate ions maintain their identity in combining with other ions to form, for example,  $\text{NH}_4\text{Br}$ ,  $(\text{NH}_4)_2\text{S}$ ,  $\text{CaSO}_4$ ,  $\text{K}_2\text{SO}_4$ , and  $(\text{NH}_4)_2\text{SO}_4$ .

Ions made from two or more atoms are called **polyatomic ions**. Other examples include the hydroxide,  $\text{OH}^-$ , the phosphate,  $\text{PO}_4^{3-}$ , and the nitrate,  $\text{NO}_3^-$ , ions.

**Polar Covalent Bonds.** A simple covalent bond is defined as a pair of electrons shared between two atoms. However, electrons are shared equally only if the atoms are the same, as is the case with diatomic molecules of the elements shown in Fig. 4-9.

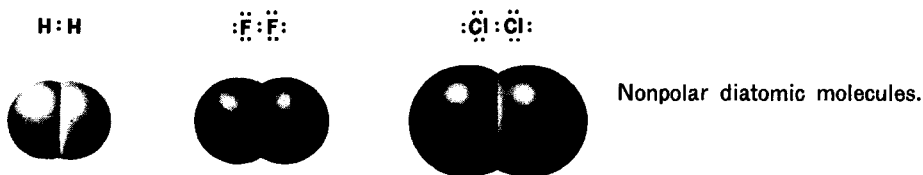


FIG. 4-9

If the atoms are different, the pair of electrons are attracted more toward one of the atoms. Such a pair of electrons constitutes a **polar bond**, making one part of a molecule partially negative and another partially positive. In the case of a diatomic molecule, this results in a **polar molecule**, which has one end relatively positive and the other relatively negative. Examples are  $\text{HCl}$  and  $\text{ClF}$ , as shown in Fig. 4-10. In these diagrams the  $\delta+$  or  $\delta-$  signifies a partial charge that

Polar diatomic molecules.  
Note that the arrow indicating polarity points toward the more electronegative of the two atoms.

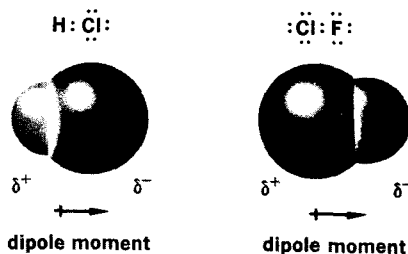


FIG. 4-10

is less in magnitude than the charge on a whole proton or electron. The arrow is used as a symbol of *polarity*, always pointing from the positive pole toward the negative.

When a diatomic molecule as a whole has a net polarity, HCl and ClF, for example, it is said to be a *dipole*; it has a *dipole moment*, which can be measured in a suitable electric field. Triatomic or other polyatomic molecules may or may not have dipole moments, depending on their structures. Consider the three molecules  $\text{H}_2\text{O}$ ,  $\text{SO}_2$ ,

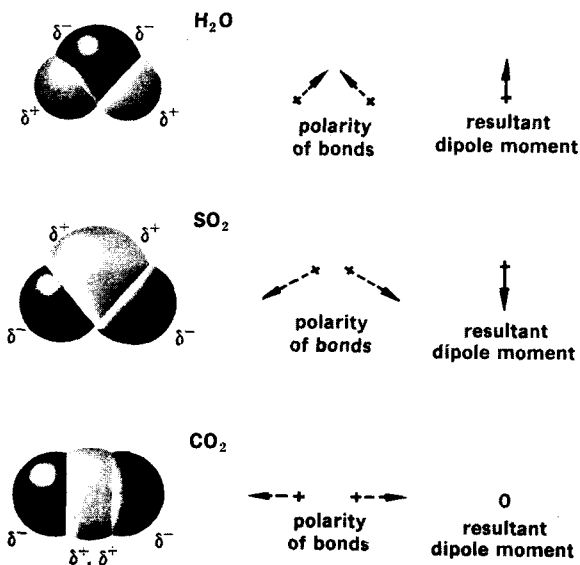


FIG. 4-11

and  $\text{CO}_2$ . The first two are polar, whereas the third is not (see Table 4-2). From X-ray and other studies it has been found that the first two molecules have angular structures, whereas  $\text{CO}_2$  is linear. Finally, in each molecule it is thought that the bonds are polar, with the electrons drawn toward the oxygen in each case. All these facts are summarized in the diagrams in Fig. 4-11. The example of  $\text{CO}_2$  is characteristic of any molecule in which the centers of positive and

# CHEMICAL CHANGES AND CHEMICAL BONDS

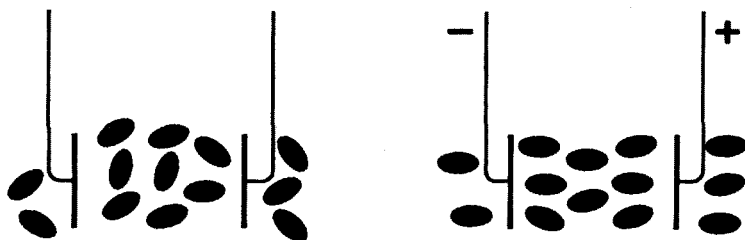


FIG. 4-12

Polar molecules become aligned in an electrical field. The tendency of the current to flow through a gas as compared to the flow through a vacuum gives a measure of the dipole moment.

negative charges coincide. Although there may be polar bonds, the polar effects of the different bonds cancel one another, leaving the molecule as a whole nonpolar.  $\text{CH}_4$  and  $\text{CCl}_4$  are also molecules in which the center of positive charge coincides with the center of negative charge (see Fig. 4-6), therefore they are nonpolar molecules, although in each of these symmetrical molecules there are four polar bonds. The polarities oppose one another geometrically, giving a resultant polarity of zero.

**EXPERIMENTAL DIPOLE MOMENTS.** The dipole moment of a molecule depends directly on the magnitude of the fractional charge, that is,  $\delta = \delta+ = \delta-$ , and on the distance separating the fractional charges. One method of determining dipole moments is based on measuring the effect that a gaseous substance has on the electric field between charged plates (see Fig. 4-12). Dipole moments are commonly expressed in debye units;<sup>1</sup> the greater the polarity of the molecule, the larger its moment in debye units.

In Table 4-2 values are given for the dipole moments of several

TABLE 4-2

formula	dipole moment, debyes*	shape of molecule	formula	dipole moment, debyes*	shape of molecule
HCl	1.1	linear	$\text{BF}_3$	0	triangular
$\text{H}_2\text{O}$	1.8	angular	$\text{CH}_4$	0	tetrahedral
$\text{SO}_2$	1.6	angular	$\text{CCl}_4$	0	tetrahedral
$\text{CO}_2$	$\sim 0^\dagger$	linear	$\text{CHCl}_3$	1.1	tetrahedral
$\text{CS}_2$	0	linear	$\text{CsF}$	7.8	linear
$\text{NH}_3$	1.5	pyramidal	$\text{CsCl}$	10.5	linear

\* Values taken from A. L. McClellan, *Tables of Experimental Dipole Moments*, W. H. Freeman and Company, San Francisco, 1963.

† The sign  $\sim$  means "approximately."

<sup>1</sup> The dipole moment unit, named for Peter Debye, the Nobel Laureate in chemistry in 1936, is defined on the basis of the magnitude of the charges and the distance separating them. A unit negative charge ( $4.8 \times 10^{-10}$  esu) and a unit positive charge ( $4.8 \times 10^{-10}$  esu) separated by a distance of 1 A constitute a dipole with a moment of:

$$\begin{aligned} \text{dipole moment} &= \text{charge} \times \text{distance} \\ &= 4.8 \times 10^{-10} \text{ esu} \times 1 \text{ A} = 4.8 \times 10^{-10} \text{ esu} \times \text{A} \\ &= 4.8 \text{ debyes (by definition)} \end{aligned}$$

$$\text{Hence, 1 debye unit} = 1 \times 10^{-10} \text{ esu} \times \text{A (or } 1 \times 10^{-18} \text{ esu} \times \text{cm)}$$

simple molecules. The two ionic cesium compounds, CsF and CsCl, are included for contrast with the other compounds that are covalent. Simple gaseous diatomic molecules of ionic compounds exist only at very high temperatures; under ordinary conditions, as we shall see in Chap. 7, ionic compounds exist as solids.

**Electronegativity.** In the foregoing discussion of polar bonds we stated that the electron pair is drawn toward one atom more than another. The power of an atom in a molecule to attract electrons is called the **electronegativity** of the atom. Studies have been made showing that, in general, the higher the ionization potential of an element, the greater its electronegativity. Also, electronegativities are calculated on the basis of the strengths of the bonds formed between atoms; the stronger the bond, the greater the difference in electronegativities. Linus Pauling has derived a scale of electronegativity values based on bond strengths. On Pauling's scale, the element fluorine, F, whose atoms have the greatest attraction for electrons, is given an arbitrary electronegativity of 4.0. All the other elements are compared with this standard; for example, potassium, K, an atom with an extremely slight affinity for electrons, has a relative electronegativity of only 0.8, whereas silicon, Si, whose electron affinity is moderate, has a value of 1.8. The higher the value, the greater the atom's attraction for an electron pair. In Fig. 4-13 the periodic variation in electronegativities with change in atomic number is shown for four periods. As the atomic number increases from 3 to 9, the electronegativity rises; but at 11, Na, it is low once more, then starts to rise till 17, Cl, is reached. (See also Table 4-3.)

As the atomic numbers increase, the electronegativities of the elements vary in a periodic way, increasing from Group I to VII in each period.

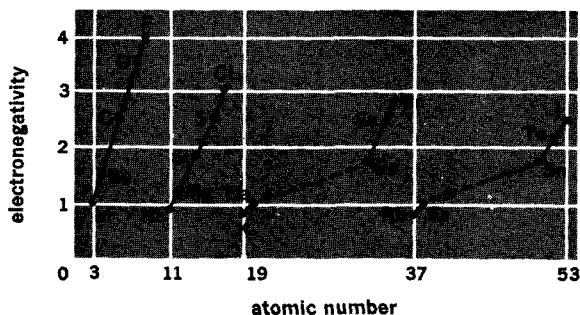


FIG. 4-13

Color and shading of diagrams of atoms, ions, and molecules throughout the text indicate the approximate relative electronegativities. The key to the shading scheme is shown in Fig. 4-15.

When two atoms of different electronegativities are joined by a covalent bond, the pair of electrons is drawn toward the atom of higher electronegativity. This results in one of the atoms being more nega-

TABLE 4-3 *Electronegativities*

IA	IIA	IVA	VIA	VIIA
Li 1.0	Be 1.5	C 2.5	O 3.5	F 4.0
Na 0.9	Mg 1.2	Si 1.8	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Ge 1.8	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Sn 1.8	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	Pb 1.8	Po 2.0	At 2.2

tive than the other and causes the bond to be polar or somewhat ionic. Pauling states that, if atoms differ sufficiently (by about 2 units) in electronegativity, they will form bonds that are mainly ionic, that is, ionic-covalent bonds. If the electronegativity difference is less than this, the bonds are mainly covalent, that is, covalent-ionic. Bonds may be covalent, covalent-ionic, ionic-covalent, or ionic.

The atoms of lowest electronegativity are those in which a new main energy level has just been started with one or two *s* electrons. The atoms of highest electronegativity are those in which a *p* sublevel is almost complete. Atoms that have partially filled *d* and *f* sublevels are intermediate in electronegativity.

## SIZES OF ATOMS, IONS, AND MOLECULES

*Covalent Radii and van der Waals Radii.* About fifty years ago X-ray methods were developed that enabled the sizes of atoms, ions, and molecules to be calculated (see Chap. 7). However, the volume occupied by a single unit of an element is difficult to represent; the shape of the orbitals is one complication; another is whether the atom is held to a neighbor by a covalent bond, as in a Cl—Cl molecule, or is just touching a neighbor, as in solid neon. However, by using a few arbitrary rules and taking advantage of modern data on the distances between atoms, the sizes of imaginary spherical atoms can be calculated. The radius of an atom is determined, not by a measurement made on an isolated single atom, but usually by measuring the distance between the nuclei of bonded atoms in a solid sample of an element. Since such atoms are bonded together, their sizes are calculated on the basis of their covalent radii for nonmetals or their metallic radii for metals. The noble gases are in a class by themselves.

The problem of assigning sizes to atoms can be illustrated by the

Covalent and van der Waals radii in a chlorine molecule. The inner circles correspond to the size of the chlorine atom represented in Fig. 4-15.

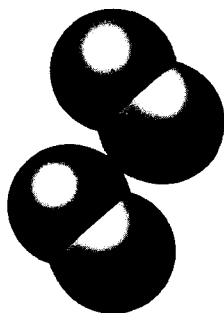
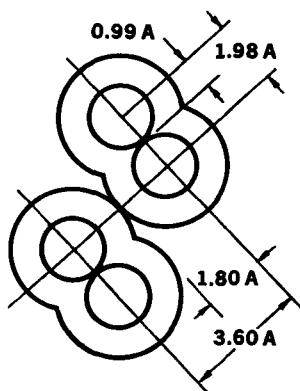


FIG. 4-14

case of elemental chlorine, as pictured in Fig. 4-14. The distance between the nuclei of two atoms bonded together is the *interatomic bonded distance*. For chlorine this is 1.98 Å; half of this distance, or 0.99 Å, is the *covalent radius* of a chlorine atom. The distance between the nuclei of two atoms in adjacent molecules is the *interatomic nonbonded distance*. For solid chlorine this is 3.60 Å; half of this distance, or 1.80 Å, is called the *van der Waals radius*, named for the Dutch physicist who studied the weak physical force of attraction between molecules which touch one another but which are not bonded chemically. This type of attraction, which is important only when molecules are very close to one another, is called the *van der Waals force*.

What size are we to assign to a chlorine atom? The radius of the bonded atom is usually of most interest to the chemist. In Fig. 4-15 the relative sizes of the spheres representing atoms of the non-metals are drawn on the basis of covalent radii. The sphere for chlorine represents a particle with a radius of 0.99 Å. Radii for atoms forming a single covalent bond range from 0.30 Å for hydrogen to 1.41 Å for antimony. The purpose of Fig. 4-15 is to show the relative volumes taken up by atoms bonded to other atoms. To visualize the size of a complete molecule, we can consider the size of the bonded atoms and then imagine expanded electron clouds reaching out as far as the van der Waals radii, as in Fig. 4-14.

**ADDITION OF COVALENT RADII.** In the pure carbon substance diamond the distance from center to center of neighboring carbon atoms is 1.54 Å. The radius of each carbon atom is  $1.54 \div 2 = 0.77$  Å.

When carbon and chlorine combine, we might expect the distance between the centers of the two atoms to be the sum of their covalent radii:

$$\begin{array}{r} 0.99 \text{ Å (chlorine radius)} \\ 0.77 \text{ Å (carbon radius)} \\ \hline 1.76 \text{ Å (sum)} \end{array}$$



# CHEMICAL CHANGES AND CHEMICAL BONDS

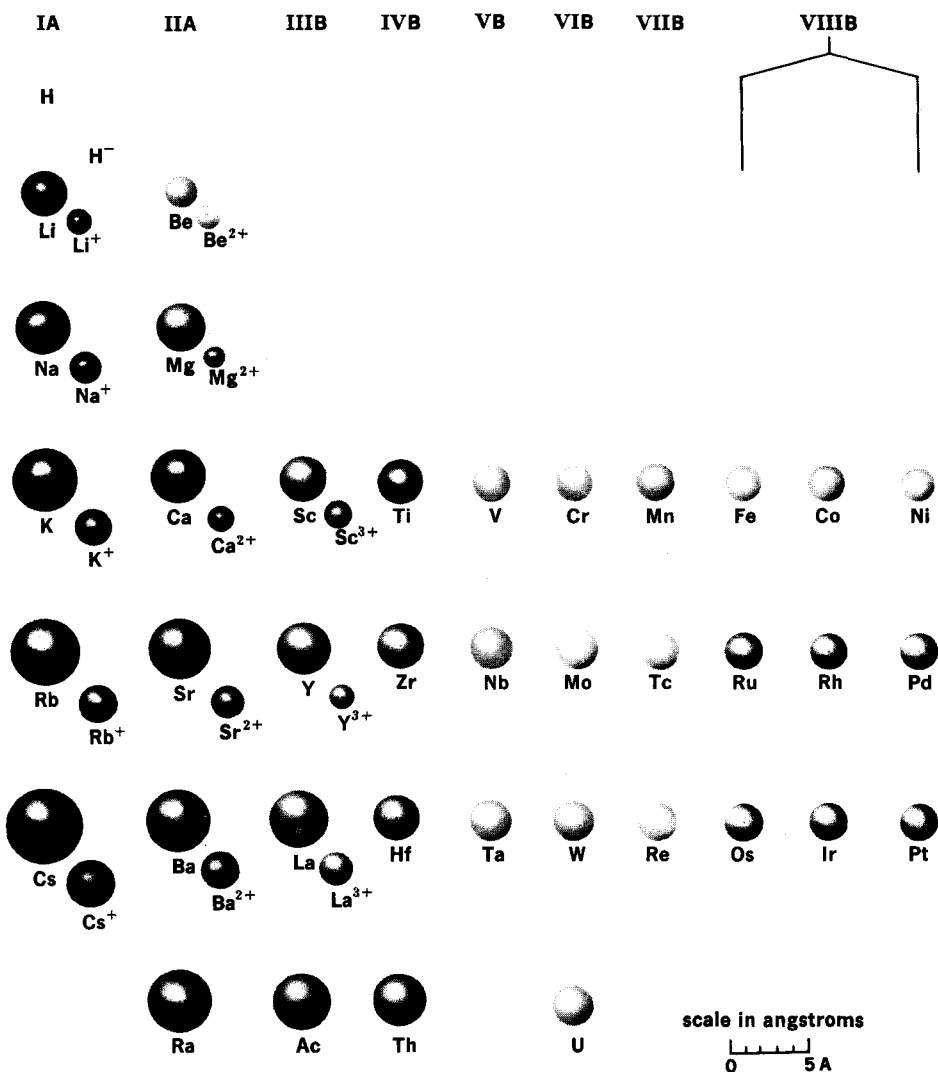
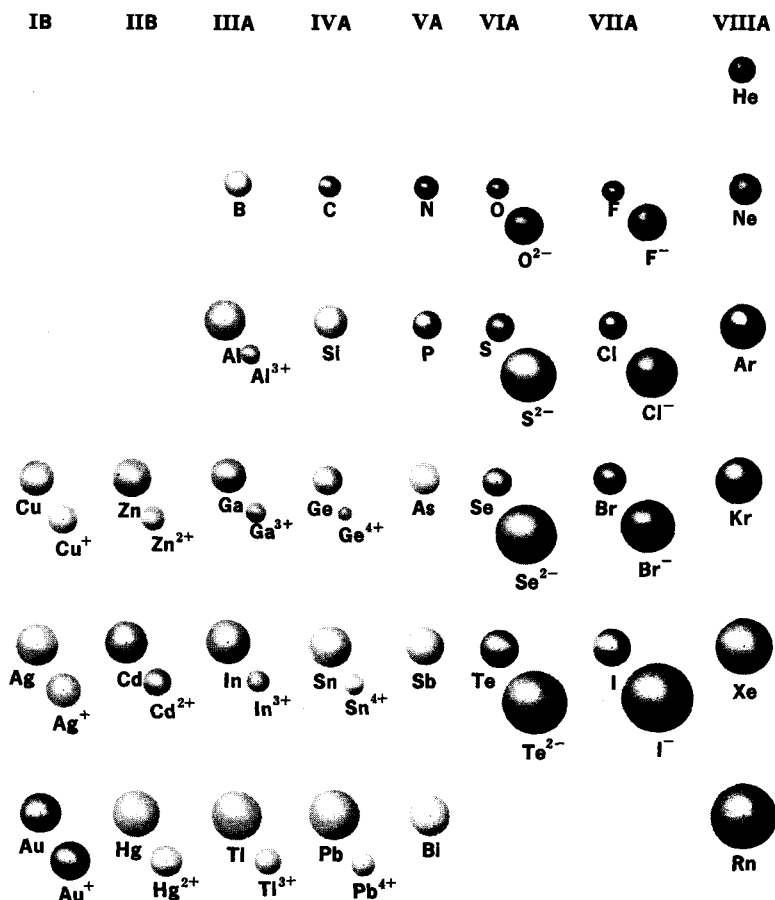


FIG. 4-15

The relative sizes of the atoms and ions of most of the elements. Electro-negativities are indicated by the color code in lower right corner. (Based on arrangement by J. A. Campbell, *J. Chem. Educ.*, **23**: 525 [1946].)

The experimentally measured C—Cl interatomic distance in the compound carbon tetrachloride,  $\text{CCl}_4$ , is 1.76 Å. The agreement between calculation and measurement is not always so perfect as this, but it is close enough to support the idea that the distance between the centers of two atoms in a molecule is the sum of their covalent radii.

# CHEMICAL CHANGES AND CHEMICAL BONDS



electronegativity scale



**Metallic Radii.** The structure of metals is taken up in more detail in Chap. 17, but we should note here that in elemental metals atoms are bonded together in such a way that we consider a pure crystal of a metal as simply a huge molecule consisting of millions of atoms held together by *metallic bonds*, which differ greatly from either ionic or covalent bonds. In metals, each atom, other than surface atoms,

commonly has either eight or twelve nearest neighbors to which it is held by metallic bonds. Half of the internuclear distance between a metal atom and one of its nearest neighbors is called its **metallic radius**. The diagrams of metal atoms in Fig. 4-15 are based on such measured metallic radii. Cesium, with a radius of 2.35 Å, is the largest atom shown.

The metallic radius of a metal atom or the covalent radius of a nonmetal atom is often referred to as the **atomic radius**.

***Ionic Radii.*** The sizes of certain ions are shown to scale in Fig. 4-15. Note that positive ions of an element are always smaller than their atoms and that negative ions are always larger. The positive hydrogen ion (a proton) is so small that it cannot be shown to scale in this figure. Note also that atoms that usually gain electrons in forming ions are toward the right of the periodic table and that atoms that usually lose electrons in forming ions are in the middle and toward the left.

The fact that positive ions are smaller than their atoms and negative ions are larger can be explained in terms of two or three effects. Outer electrons are not only attracted by the positive nucleus but are repelled by electrons in lower energy levels and in their own level. This repulsion, which has the result of reducing the *effective nuclear charge*, is called the **shielding or screening effect**. When an atom gains one or more electrons, the number of electrons in the outer energy level is increased, and each electron is somewhat more effectively screened from the nucleus. These outer electrons repel one another, and since the effective nuclear charge is less, they force one another farther from the nucleus. The result is that a negative ion is larger than its atom. In accounting for the relative sizes of positive ions, one needs to consider, in addition to changes in the screening effect, the fact that often all the electrons in the outermost energy level are lost, so that the large electron clouds due to these electrons disappear. The overall result is a positive ion that is smaller than the initial atom.

At the left of Fig. 4-15 are the atoms of low electronegativity, which tend to lose electrons and form small positive ions. Note that the larger the positive charge, the smaller the ion. At the right of the figure are the atoms of high electronegativity, which tend to gain electrons and form large negative ions. Note that the larger the negative charge, the larger the ion. Figure 4-16 shows this trend in size very clearly by comparing particles that have the same number of electrons and the same number of electron shells but different charges on their nuclei.

***Electronegativity and Atomic Size.*** In Fig. 4-15 differences in color and shading indicate the approximate relative electronegativities of the elements. For nonmetals, the deeper the color, the higher the

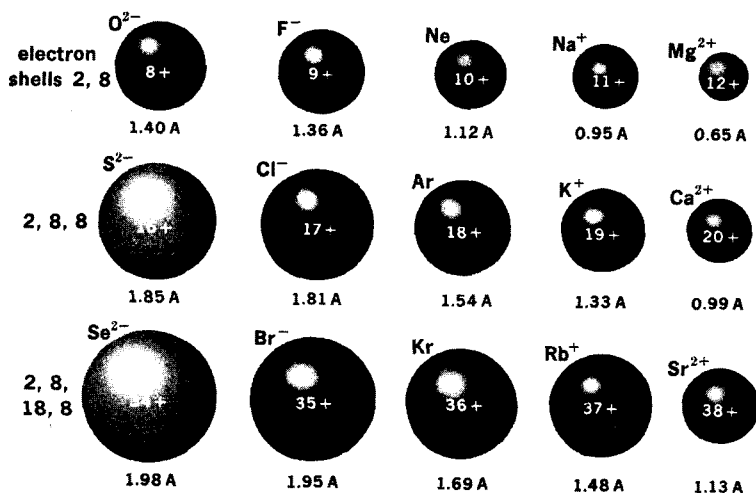


FIG. 4-16

For atoms or ions with the same number of electrons, the size decreases as the positive charge on the nucleus increases.

electronegativity, reaching a maximum of 4.0 at fluorine, F; for metals, an increase in shading indicates a decrease in electronegativity, reaching a minimum of 0.7 at cesium, Cs. Numerical values for certain other elements can be seen in Table 4-3 and compared with the shading of their atoms in Fig. 4-15. The general trends are easily seen. Atomic size generally decreases and electronegativity increases from left to right in a given period; size increases and electronegativity decreases from top to bottom in the A families of the periodic table.

## SUMMARY

We have taken up so much material in this and preceding chapters about atoms and the way in which they combine that we should really pause and consolidate our gains.

First, we should recognize that much of our discussion has been in the realm of theory. We can interpret such phenomena as those observed in the cathode-ray tube, in the mass spectrograph, and in chemical reactions in terms of atoms composed of protons, neutrons, and electrons. But we must remember that the experimental evidence for these bits of matter is not so direct as that for the existence of a virus or a distant star. We have good reason to expect that further research will bring new knowledge and that our present theories might be changed. What are the main ideas with which we have become familiar to this point?

1. There are just over 100 elements now known.
2. A compound is a substance made from two or more elements

## CHEMICAL CHANGES AND CHEMICAL BONDS

in which the original atoms of the elements have reacted chemically with one another in a definite whole-number ratio.

3. The manner in which an element combines depends mainly on the number of electrons in the outside energy level of the atoms of the element.

4. When a chemical reaction occurs, we think atoms have acted on one another by transferring or sharing electrons or both.

5. The particles in compounds are held together by chemical bonds. These bonds may be ionic or covalent or intermediate in character.

6. We may generalize and say that a chemical reaction occurs when, and only when, a chemical bond is formed or broken.

7. When unlike atoms share a pair of electrons, the electrons are drawn toward the atom of higher electronegativity, and a polar covalent bond results.

8. When a molecule is formed, if the center of negative charge does not coincide with the center of positive charge, the molecule is polar. For many molecules, the dipole moment has been measured experimentally.

## CHAPTER REVIEW

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### *Terms*

Properties and chemical change, sublimates, synthesis, composition and chemical change, limitations of law of definite composition, energy and chemical change, exothermic, endothermic, valence, valence electron, metal, nonmetal, metalloid, noble gas, transfer of electrons, sharing of electrons, chemical equation, reactant, product, electronic structure of ions, rule of eight, limitations of rule of eight, molecule, bonding orbital, molecular orbital, sigma orbital, sigma bond, pi orbital, pi bond, bond energy, hybridized orbital, Lewis electron-dot formula, electrovalent bond, ionic bond, polyatomic ions, covalent bond, polar covalent bond, polar molecule, dipole, dipole moment, debye unit, shapes of molecules, electronegativity, covalent radius, van der Waals radius, metallic radius, atomic radius, ionic radius, shielding or screening effect, effective nuclear charge, electronegativity, atomic size.

### *Exercises*

1. Make a list of chemical reactions that you can observe in or about your home.
2. What is the percentage by weight, calculated to four significant figures, of chlorine in  $^{23}\text{Na}^{37}\text{Cl}$ ; in  $^{23}\text{Na}^{35}\text{Cl}$ ? The masses of  $^{23}\text{Na}$ ,  $^{35}\text{Cl}$ , and  $^{37}\text{Cl}$  are 22.99, 34.97, and 36.97, respectively. Would either of these answers represent the percentage of chlorine in a sample of natural salt,  $\text{NaCl}$ ? Explain.

3. Using a periodic table, place each of the following elements into one of the four classes: rubidium, xenon, tantalum, tellurium, fluorine, sulfur, rhenium.
4. Locate in the periodic table the elements that are composed of atoms in which the highest sublevel with partly or completely filled orbitals is an *s* sublevel.
5. Locate in the periodic table the elements that are composed of atoms in which the highest *p* sublevel lacks only one or two electrons of being filled.
6. When an element described in Exercise 4 reacts with an element described in Exercise 5, what type or class of compound is likely to form? What takes place within the atoms to bring about the formation of the compound? Are your answers here subject to some qualification? (See discussion on electronegativity.)
7. State specifically how an atom of each of the following elements differs from the ion that it is likely to form when it reacts to form an ionic compound: strontium, bromine, selenium, oxygen, potassium, iodine, barium.
8. The formulas for cesium chloride, barium chloride, and gallium chloride are  $\text{CsCl}$ ,  $\text{BaCl}_2$ , and  $\text{GaCl}_3$ , respectively. Justify each formula by means of atomic theory. What would tend to prohibit the formation of  $\text{CsCl}_2$ ?
9. Explain why the composition of a pure compound shows little or no variation, although samples are obtained from widely spaced points on the earth's surface.
10. There are two well-known iron chlorides:  $\text{FeCl}_2$  and  $\text{FeCl}_3$ . Is this a violation of the law of definite composition? Explain.
11. When calcium reacts with oxygen, heat energy is liberated to the surroundings. How can we account for the production of the heat? What special term is used to describe reactions that liberate heat?
12. Atoms of hydrogen react violently with one another, with the evolution of much heat to form hydrogen molecules,  $\text{H}_2$ . Diagram the bonding orbital in a molecule of  $\text{H}_2$ . What term is used to refer to this type of bonding orbital?
13. Chlorine atoms also react with one another to form molecules,  $\text{Cl}_2$ . Sketch or diagram the bonding orbital.
14. Do the terms covalent bond and sigma bond have precisely the same meaning? Explain.
15. Molecules of  $\text{H}_2$  and  $\text{Cl}_2$  are properly called covalent molecules. May they also be properly called covalent compounds? Why?
16. Using electron-dot formulas, represent stable molecules of the following compounds: silicon hydride (compound of Si and H); phosphorus hydride (P and H); carbon bromide (C and Br); bromine iodide (Br and I).
17. Given two compounds, say calcium oxide ( $\text{CaO}$ ) and mercury oxide ( $\text{HgO}$ ), how could one proceed experimentally to find out something about the relative sizes of their bond energies?

## CHEMICAL CHANGES AND CHEMICAL BONDS

18. Consider the molecule  $\text{CF}_4$ , carbon tetrafluoride. Much experimental evidence establishes this molecule as covalent, nonpolar, and a tetrahedrally shaped molecule with carbon at the center and bonded to fluorine at the corners by four equivalent bonds. What problems arise when we attempt to account for these characteristics of the  $\text{CF}_4$  molecule in terms of a model employing bonding orbitals of fluorine atoms to overlap the unfilled  $p$  orbitals of an isolated or ground-state carbon atom? How do we get around these difficulties?
19. What conditions give rise to a polar bond; to a polar molecule?
20. Carbon tetrachloride,  $\text{CCl}_4$ , has a dipole moment of zero, and chloroform,  $\text{CHCl}_3$ , has a moment of 1.1 debyes. Why?
21. Would you expect the bonds of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  to be polar or nonpolar? Why? Water has a dipole moment of 1.8 debyes, and carbon dioxide has a zero dipole moment. Why?
22. Explain how tables of electronegativity may be used to help predict the degree of polarity of a bond.
23. What is meant by ionic-covalent and covalent-ionic bonds?
24. In which of the following compounds are the bonds mainly covalent and in which are they mainly ionic:  $\text{NH}_3$ ,  $\text{PBr}_3$ ,  $\text{CaF}_2$ ,  $\text{CaI}_2$ ,  $\text{RbCl}$ ,  $\text{Rb}_2\text{O}$ ,  $\text{SiO}_2$ ?
25. Calculate the bond length, that is, the distance between nuclei of two bonded atoms, for bromine fluoride from their covalent radii: F, 0.64 Å; Br, 1.14 Å. Calculate the approximate overall length of a Br-F molecule. The van der Waals radii are F, 1.35 Å; Br, 1.95 Å. Sketch this molecule to scale in a way comparable with Fig. 4-14.

## SUPPLEMENTARY READING

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# FORMULAS AND EQUATIONS; CLASSES OF COMPOUNDS



The number of known compounds is estimated at well over 1 million. To become familiar with just a small fraction of this number is a huge task indeed, although the compounds are arranged in classes according to their common characteristics and then named in a systematic manner. In a one-year chemistry course only a few classes of compounds are discussed. We may expect, however, to become familiar with members of the more common classes, to be able to name them systematically and to write their formulas, to understand their chemical nature, and to appreciate their economic importance.

## FORMULAS

The composition of a compound is shown by means of a formula. For example, the formula for potassium nitrate,  $\text{KNO}_3$ , shows that this substance is made up of combined potassium, nitrogen, and oxygen. Also, it shows that one atom of potassium, one of nitrogen, and three of oxygen are united chemically to make a small unit of the compound. Whether this small unit is a covalent molecule or a cluster of ions is not apparent from the formula.

**Oxidation Numbers.** A system of small whole numbers related to the combining ratios of elements is useful in helping us remember formulas for compounds and in correlating certain chemical phenomena. The **valence numbers** long served this purpose. Because the valence of an element has been defined in a variety of ways during the past 100 years and because there has been a tendency to relate valence to valence electrons, electrovalence, and covalence, it has



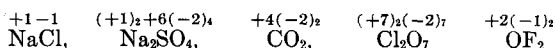
become difficult to assign agreed-on valence numbers. In their place a set of numbers obtained by arbitrary rules and called **oxidation numbers** or **oxidation-state numbers** has been established.

The system of oxidation numbers has been developed during a period of years from a consideration of (1) the composition of compounds, (2) the relative electronegativities of the elements comprising the compounds, and (3) arbitrary rules and guides.

Three of the arbitrary rules are:

1. The oxidation state of an uncombined element is zero.
2. In a compound the more electronegative elements are assigned negative oxidation states, and the less electronegative elements are assigned positive states.
3. In a formula for a compound the sum of the positive oxidation states equals the sum of the negative oxidation states.

Examples of assigned oxidation numbers are:



*The Periodic Table and Oxidation Numbers.* We can formulate some general guides based on the periodic table that will be helpful in predicting oxidation numbers of some of the common elements when in chemical union. Note that the oxidation number of an ion is the same as the charge of the ion. The oxidation number of an atom in a covalent compound does not necessarily correspond with the number of covalent bonds joining the atom to other atoms.

1. The metals in the A family of group I have oxidation states of +1 in compounds. For example, NaCl and KCl are compounds in which sodium and potassium have oxidation numbers of +1. Hydrogen has an oxidation state of +1 when combined with nonmetals and -1 when combined with metals.

The members of the B family of group I have several oxidation states. Among these, we should remember that silver has a +1 oxidation state and that copper is usually present in compounds with a +2 oxidation state, although compounds in which copper exhibits a +1 oxidation state are not uncommon.

2. The members of both the A and B families of group II commonly exhibit a +2 oxidation state. Thus, in  $\text{MgCl}_2$ ,  $\text{CaBr}_2$ ,  $\text{ZnSO}_4$ , and  $\text{Hg}(\text{NO}_3)_2$ , the oxidation state of the metal is +2. Because these all represent electrovalent compounds, the metallic ions have 2 plus charges, for example,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ . Mercury, in the B family, also forms compounds in which its oxidation state is +1, for example,  $\text{Hg}_2\text{Cl}_2$ .

3. Aluminum, in group IIIA, has an oxidation state of +3. Examples:  $\text{AlCl}_3$ ,  $\text{Al}(\text{NO}_3)_3$ .

4. Tin and lead, in group IVA, have oxidation states of +2 or +4. Examples:  $\text{SnCl}_2$ ,  $\text{SnCl}_4$ ,  $\text{PbCl}_2$ ,  $\text{PbCl}_4$ .

Carbon, in group IVA, commonly has oxidation states of +4 or -4.

Examples:  $\text{CH}_4$ ,  $\text{CO}_2$ . However, the assignment of oxidation states to carbon can be very involved.

5. The nonmetals of the A family of group V often have oxidation states of  $-3$  or  $+5$ . Example of  $-3$ :  $\text{NH}_3$ . Example of  $+5$ :  $\text{N}_2\text{O}_5$ . (Many other oxidation states are commonly displayed by these elements.)

6. The nonmetals of the A family of group VI often have oxidation states of  $-2$  and  $+6$ ; in rare cases,  $-1$ . Examples of  $-2$ :  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{CaO}$ ,  $\text{ZnS}$ . Example of  $+6$ :  $\text{SO}_3$ . Group VIA elements also form compounds with a  $+4$  oxidation state, for example,  $\text{SO}_2$ . Because oxygen has the second highest electronegativity (3.5), it almost always has an oxidation number of  $-2$ ; in rare cases,  $-1$ , for example,  $\text{H}_2\text{O}_2$ ; only in fluorine-containing compounds is oxygen's oxidation number positive.

7. The nonmetals of the A family of group VII have oxidation states of  $-1$  when combined with hydrogen or metals. Examples:  $\text{HCl}$ ,  $\text{NaBr}$ ,  $\text{ZnI}_2$ . (Some of them also display oxidation states of  $+7$ ,  $+5$ ,  $+3$ , and  $+1$ .)

SUMMARY. Common oxidation states for a number of elements are shown in Fig. 5-1. Oxidation numbers that we can predict from the periodic table at this stage, noting that we are on safer ground with A families, are:

group	I	II	III	IV	V	VI	VII
oxidation number	+1	+2	+3	+2, +4 -4	+5 -3	+6 -2	+7 -1

Because the sum of the oxidation states for all the components of a compound is zero, we can calculate the oxidation state of an un-

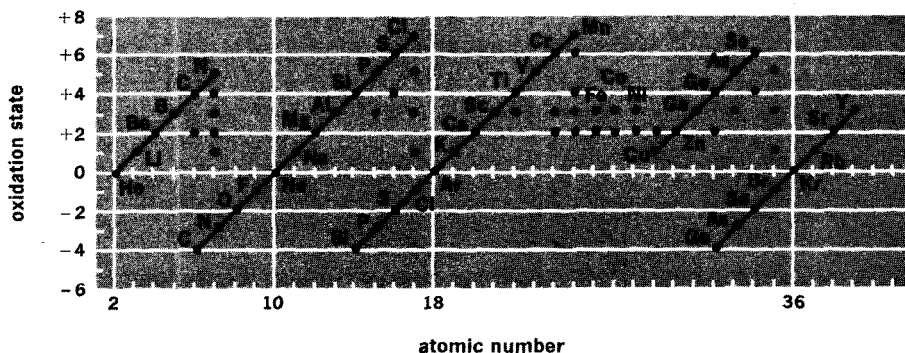


FIG. 5-1

From the periodic law we would expect oxidation numbers to be a periodic function of the atomic numbers. Study of this graph reveals that this is indeed the case, particularly for the maximum and minimum states (through which the lines have been drawn for emphasis). It is important to note that an element may have a number of oxidation states which are not evident from its position in the periodic table.

familiar element in a compound provided we know the formula for the compound and the oxidation states of all the other elements in it.

**PROBLEM 1** What is the oxidation state of gold in gold chloride,  $\text{AuCl}_3$ ?

*Solution* Because the chloride ion has an oxidation state of  $-1$ , the oxidation state of gold must be  $+3$ :  $\text{AuCl}_3$ ,  $+3(-1)_3$   $+3 + (-3) = 0$ .

**PROBLEM 2** What is the oxidation state of tellurium in tellurous acid,  $\text{H}_2\text{TeO}_3$ ?

*Solution* If we assume the oxidation states of hydrogen and oxygen are  $+1$  and  $-2$ , respectively, the oxidation state of tellurium is  $+4$ :  $\text{H}_2\text{TeO}_3$ ,  $(+1)_2 + 4(-2)_3$   $(+2) + (+4) + (-6) = 0$ .

It should be borne in mind that the oxidation-state numbers do not imply isolated charges. For example, in the compound  $\text{NO}$  the oxidation state of oxygen is  $-2$ , although oxygen is covalently bonded to nitrogen and no ions are present; in the compound  $\text{CaO}$  the oxidation state of oxygen is also  $-2$ , but the oxygen in this compound is in the form of ions, each with a doubly negative charge,  $\text{O}^{2-}$ . We shall follow the plan of designating the oxidation numbers by placing a  $-$  or  $+$  in front of the number; to show the magnitude of the charge on an ion, the number precedes the  $+$  or  $-$  sign, except that the number 1 is not written. Examples:  $\text{Cl}^-$ ,  $\text{O}^{2-}$ ,  $\text{Al}^{3+}$ .

**Polyatomic Ions.** Many ions are composed of two or more atoms, for example,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ . Because they occur so often in common substances, the student should memorize the formula and oxidation state (or charge) of each of the following ions: nitrate,  $\text{NO}_3^-$ ; hydroxide,  $\text{OH}^-$ ; acetate,  $\text{C}_2\text{H}_3\text{O}_2^-$ ; carbonate,  $\text{CO}_3^{2-}$ ; sulfate,  $\text{SO}_4^{2-}$ ; phosphate,  $\text{PO}_4^{3-}$ ; and ammonium,  $\text{NH}_4^+$ .

**Formulas from Oxidation Numbers.** In using oxidation numbers to deduce the formula of a compound, we choose the simplest ratio of atoms or ions that makes the plus and minus oxidation numbers add to zero.

This ratio is 1:1 when the oxidation state of one component equals that of a second. A component refers to a simple ion, such as  $\text{Na}^+$ ,  $\text{O}^{2-}$ , or  $\text{Cl}^-$ , or to a covalently bonded atom, such as  $\text{H}$  or  $\text{Cl}$  in  $\text{HCl}$ , or to a polyatomic ion, such as  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ . Examples:  $\text{NaCl}$  or  $\text{NaCl}$ ;  $\text{HCl}$  or  $\text{HCl}$ ;  $\text{MgO}$  or  $\text{MgO}$ ;  $\text{Cu}(\text{SO}_4)$  or  $\text{CuSO}_4$ ;  $\text{Al}(\text{PO}_4)$  or  $\text{AlPO}_4$ ;  $(\text{NH}_4)(\text{NO}_3)$  or  $\text{NH}_4\text{NO}_3$ .

The ratio is 1:2 when the oxidation state of one is twice that of the other. Examples:  $\text{CaCl}_2$  or  $\text{CaCl}_2$ ;  $\text{Na}_2\text{SO}_4$  or  $\text{Na}_2\text{SO}_4$ ;  $\text{CO}_2$  or  $\text{CO}_2$ ;  $\text{H}_2\text{O}$  or  $\text{H}_2\text{O}$ ;  $\text{SnO}$  or  $\text{SnO}_2$ ;  $(\text{NH}_4)_2(\text{CO}_3)$  or  $(\text{NH}_4)_2\text{CO}_3$ .

The ratio is 1:3 when the oxidation state of one is three times that

of the other. Examples:  $\overset{+3}{\text{Fe}}\overset{-1}{\text{Br}}\overset{-1}{\text{Br}}\overset{-1}{\text{Br}}$  or  $\overset{+1}{\text{Fe}}\overset{+1}{\text{Br}}_3$ ;  $\overset{+1}{\text{H}}\overset{+1}{\text{H}}\overset{-3}{\text{H}}(\text{PO}_4)$  or  $\text{H}_3\text{PO}_4$ .

The ratio is 2:3 when one has an oxidation state of 3 and the other of 2. Examples:  $\overset{+3}{\text{Al}}\overset{+3}{\text{Al}}\overset{-2}{\text{O}}\overset{-2}{\text{O}}$  or  $\text{Al}_2\text{O}_3$ ;  $\overset{+2}{\text{Mg}}\overset{+2}{\text{Mg}}\overset{-3}{\text{Mg}}\overset{-3}{\text{N}}\overset{-3}{\text{N}}$  or  $\text{Mg}_3\text{N}_2$ ;  $\overset{+2}{\text{Ca}}\overset{+2}{\text{Ca}}\overset{-3}{\text{Ca}}(\text{PO}_4)(\text{PO}_4)$  or  $\text{Ca}_3(\text{PO}_4)_2$ .

Other ratios, such as 1:4, 1:5, 2:5, and 2:7, are not uncommon. For example, in a certain oxide of chlorine, the oxidation states of chlorine and oxygen are +7 and -2, respectively. Accordingly, the simplest formula is  $\text{Cl}_2\text{O}_7$ , the simplest ratio in which the oxidation states add to zero:  $[2 \times (+7)] + [7 \times (-2)] = 0$ .

The formulas for electrovalent compounds can be predicted from the oxidation numbers of their elements. But note that, although the formulas for electrovalent compounds ordinarily indicate merely the simplest ratio of ions, the formulas for covalent molecules show the actual number of atoms that have combined to form a molecule. That the molecule may or may not be formed by the union of the smallest possible number of atoms is shown in the following examples:  $\text{NH}_3$ , ammonia;  $\text{CO}_2$ , carbon dioxide;  $\text{H}_2\text{O}_2$ , hydrogen peroxide;  $\text{C}_6\text{H}_6$ , benzene;  $\text{P}_4\text{O}_{10}$ , phosphorus pentoxide;  $\text{C}_2\text{H}_2$ , acetylene. It is not usually possible to predict the formula of a covalent compound on the basis of oxidation states.

## INTRODUCTION TO SYSTEMATIC NAMING OF COMPOUNDS

The formula of a simple compound is usually written so that the least electronegative element is indicated first and the most electronegative element last. In naming the substance, the least electronegative element is usually mentioned first.

### *Compounds Containing Two Elements (Binary Compounds).*

The name shows the two elements present and ends in *-ide*. Examples:

$\text{H}_2\text{O}$	hydrogen oxide
$\text{HCl}$	hydrogen chloride
$\text{K}_2\text{S}$	potassium sulfide
$\text{AlBr}_3$	aluminum bromide

Although the names of binary compounds end in *-ide*, many compounds that contain more than two elements are also named in this manner. Metallic hydroxides and ammonium compounds of the type  $\text{NH}_4\text{X}$ , where X is a simple negative ion, are two cases in which the compounds are so named:

$\text{Ca}(\text{OH})_2$	calcium hydroxide (not a binary compound)
$\text{NH}_4\text{Cl}$	ammonium chloride (not a binary compound)

*Compounds Containing Three Elements, One of Which Is Oxygen.* There are several classes of compounds that contain oxygen and two other elements. A very common one is the *-ate* class. The two

## FORMULAS AND EQUATIONS; CLASSES OF COMPOUNDS

elements other than oxygen are indicated in the name, and the name ends in *-ate*. Examples:

$\text{H}_2\text{SO}_4$	hydrogen sulfate
$\text{HNO}_3$	hydrogen nitrate
$\text{Na}_2\text{SO}_4$	sodium sulfate
$\text{NaClO}_3$	sodium chlorate

Another common class is the *-ite* class:

$\text{H}_2\text{SO}_3$	hydrogen sulfite
$\text{HNO}_2$	hydrogen nitrite
$\text{Na}_2\text{SO}_3$	sodium sulfite
$\text{NaClO}_2$	sodium chlorite

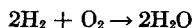
Other classes are discussed in later chapters.

***Oxidation Numbers and Names of Compounds.*** Certain elements share or transfer their electrons in more ways than one; hence these elements have more than one oxidation number. For example, iron forms two series of compounds, one in which its oxidation number is +2 and another in which it is +3. To give these compounds unambiguous names, the oxidation number is indicated with roman numerals, thus:  $\text{FeCl}_2$ , iron(II) chloride;  $\text{FeCl}_3$ , iron(III) chloride;  $\text{FeSO}_4$ , iron(II) sulfate;  $\text{Fe}_2(\text{SO}_4)_3$ , iron(III) sulfate. Copper also has two oxidation states in compounds, namely, +1 and +2. For example,  $\text{CuCl}$ , copper(I) chloride;  $\text{CuCl}_2$ , copper(II) chloride. Because copper(I) compounds are not common, it is customary to omit the oxidation number in the name of copper(II) compounds. Therefore, if no oxidation state is shown, it is assumed that the copper(II) compound is meant.

Unfortunately for the student of chemistry, the method of naming just described is of recent origin, and many common compounds were already named in accordance with other systems. Thus  $\text{CuCl}$ ,  $\text{FeCl}_2$ ,  $\text{CuCl}_2$ , and  $\text{FeCl}_3$  are called cuprous chloride, ferrous chloride, cupric chloride, and ferric chloride, respectively. These older names persist, which means that the student is sometimes faced with the necessity of knowing two or more names for a single compound.

## CHEMICAL EQUATIONS

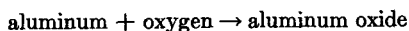
Equations are used to represent chemical reactions. The equation



states that hydrogen and oxygen react to form water. It further states that for each molecule of oxygen, two molecules of hydrogen are required and two molecules of water result. The formulas show the composition of the reacting molecules and of the resulting molecules. Because we know the weights of these molecules, we can determine weight relationships for the reaction.

There are three distinct steps in writing an equation. They are illustrated by two examples, the first showing the reaction of aluminum and oxygen, the second showing the reaction of iron(III) sulfate and calcium chloride.

*Step 1.* Show in words on the left side of the arrow the substances that are brought together and on the right those which are formed. Use a plus sign to separate the different substances:

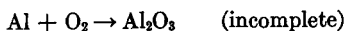


*Step 2.* Write the correct formula for each of the substances mentioned in the word equation.

*a. Elemental* substances are usually shown in equations as monatomic molecules. (Their symbols require no subscript.) Some notable exceptions are the diatomic molecules  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$ .

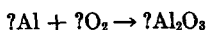
*b. Compound* substances have formulas that can often be obtained from the oxidation numbers of the elements in the compounds.

In the equation that we have begun, the molecules of aluminum and oxygen must be represented, respectively, as monatomic and diatomic (see [a] above), and the formula of aluminum oxide is shown as  $\text{Al}_2\text{O}_3$  (see [b] above). Consequently,

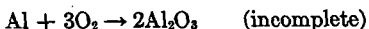


*Step 3.* Balance the incomplete equation. This is done by putting numbers *in front* of the formulas so that the same number and kinds of atoms will be represented on the right of the arrow as on the left.

A most important thing to remember is that none of the subscript numbers, shown correctly in step 2, can be changed in order to balance the equation:



It will be noted that the number of oxygen atoms must be divisible by both 2 and 3, because each  $\text{O}_2$  molecule contains 2 atoms of oxygen and each  $\text{Al}_2\text{O}_3$  unit contains 3 atoms of oxygen. The smallest number divisible by both 2 and 3 is 6. In our equation we show 3 oxygen molecules (6 atoms of oxygen) and 2 aluminum oxide units (6 atoms of oxygen, because each unit contains 3):

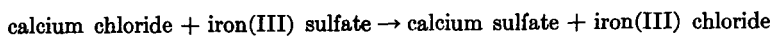


As the equation now stands, 4 atoms of Al are represented on the right and only 1 on the left. We must also show 4 on the left. The finished equation is

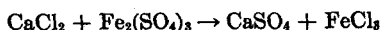


The second example follows.

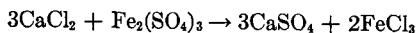
*Step 1*



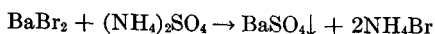
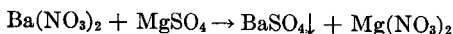
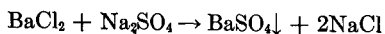
*Step 2*



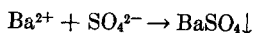
Step 3



**Ionic Equations.** In many chemical reactions involving ionic compounds in water solutions, only two species of ions participate in a particular reaction. This point is illustrated by the following equations, which represent three seemingly different reactions that are carried out in water solutions. The downward arrow indicates that a compound is not soluble and separates or precipitates from the solution.



As far as the formation of insoluble barium sulfate is concerned, these three reactions all require that barium ions and sulfate ions come together to form insoluble  $\text{BaSO}_4$ . Hence, the single observable chemical change for the reactions above could be represented as



This type of equation is called an ionic equation. Note that the charges add to zero.

## MOLE

In many kinds of chemical problems, it is necessary to consider quantities of substances in terms of the number of atoms, ions, or molecules present. For example, if we compare the amounts of heat liberated by different chemical reactions, our comparisons have more meaning when the heats are measured for reactions in which the same numbers of atoms, molecules, or ions react.

The unit devised by chemists to express numbers of atoms, ions, or molecules is called the mole. A **mole** is defined as that quantity of a substance that contains the same number of ultimate particles (atoms, molecules, ions, or units of ions) as are contained in 12 g of carbon-12. The purpose of relating our unit number of particles to the standard of atomic weights is to provide a ready method of calculating the weight of a mole of any substance (**molar weight**).

Suppose one is asked to calculate the weight of a dozen golf balls or of a dozen baseballs. To make the calculation, one would need the average weight of a golf ball or baseball; he would then multiply by 12 to get the total weight of a dozen. The same method could be used to calculate the weight of a mole of silver, or of copper, or of any other substance. But a much simpler method is available that does not involve knowing either the weights of single atoms or the number of atoms in a mole. We can simply refer to a table of *relative*

atomic weights and see how the weight in grams of a mole of any element compares with 12 g of carbon-12. The following examples will show how this comparison is made.

Consider a mole of carbon-12 atoms and a mole of magnesium atoms. By definition, a mole of  $^{12}\text{C}$  is 12 g of this substance. What weight of magnesium atoms contains the same number of atoms as are present in the 12 g of carbon-12? We see from a table of atomic weights that the average weight of magnesium atoms is 24.31 awu. Because each magnesium atom is slightly more than twice as heavy as a single carbon atom, it follows that a mole of magnesium weighs slightly more than twice the weight of a mole of  $^{12}\text{C}$ , or 24.31 g, precisely. This quantity, 24.31 g of magnesium, contains the same number of atoms as are contained in 12 g of  $^{12}\text{C}$  and is referred to as a *mole of magnesium*.

Let us consider additional examples. The weights of hydrogen, oxygen, and sulfur atoms are 1.008 awu, 15.999 awu, and 32.06 awu, respectively, on the scale  $^{12}\text{C} = 12$  awu. It follows that 1.008 g of hydrogen, 15.999 g of oxygen, or 32.06 g of sulfur each contains the same number of atoms as are contained in 12 g of  $^{12}\text{C}$ . These are the weights of a mole of hydrogen atoms, oxygen atoms, or sulfur atoms, respectively.

The mole concept is not limited to atoms. We may also apply it to matter in which the ultimate particles are molecules, ions, or units of ions. For example, a mole of oxygen molecules ( $\text{O}_2$ ) weighs 31.998 g, and a mole of ozone molecules ( $\text{O}_3$ ) weighs 47.997 g. Each contains the same number of molecules as there are atoms in a mole of carbon-12.

Our guide to the weight of a mole is the formula for the substance. Suppose we wish to find the weight of a mole of aluminum fluoride,  $\text{AlF}_3$ . The simplest unit of this compound is one aluminum ion ( $\text{Al}^{3+}$ ) and three fluoride ions ( $\text{F}^-$ ,  $\text{F}^-$ ,  $\text{F}^-$ ). The weight of this unit is  $26.98 + 3(18.998)$  or 83.974 awu. The weight of  $\text{AlF}_3$ , which contains as many  $\text{AlF}_3$  units as there are atoms in 12 g of  $^{12}\text{C}$ , is 83.974 g. This quantity is a mole of  $\text{AlF}_3$ .

We may summarize. To find the weight of a mole of a substance, first write its formula. Second, add the atomic weights to get the weight of a single unit indicated by the formula. This formula weight expressed in atomic weight units is the weight of a single atom, or molecule, or unit of ions as indicated by the formula. The formula weight expressed in grams is the weight of a mole of the substance. Some authors refer to the weight of a mole as a gram-mole.<sup>1</sup> See Table 5-1 and Fig. 5-2 for additional examples.

Modern experimental methods for counting atoms, ions, and molecules show that in one mole of a substance there are  $6.0228 \times 10^{23}$

<sup>1</sup> The formula weight expressed in pounds is a pound-mole; that is, a pound-mole of  $^{12}\text{C}$  is 12 lb, of  $\text{CO}_2$ , 44.009 lb. In this country, quantities are often expressed in terms of the pound-mole in the chemical industry. Because 1 lb = 454 g, a pound-mole contains 454 times as many particles as a mole.



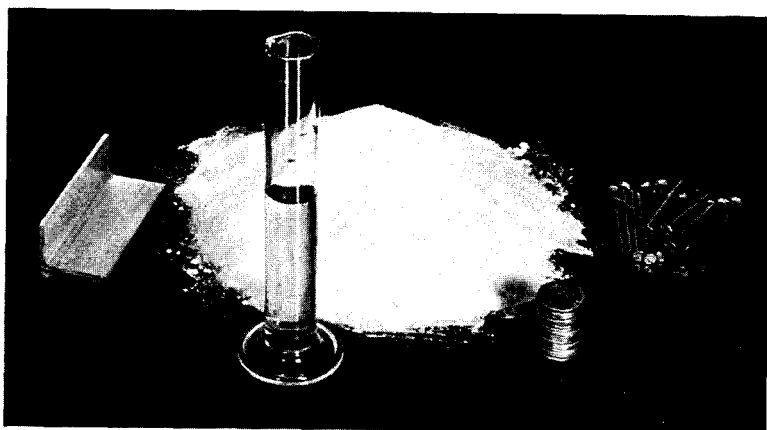


FIG. 5-2

Arranged from left to right around 1 mole of sugar (342 g) are 1 mole of aluminum (27 g), 1 mole of water (18 g), 1 mole of copper (64 g), and 1 mole of iron (56 g). Each sample contains  $6 \times 10^{23}$  atoms if an element, or that number of molecules if a compound.

particles or formula units. This huge number is called **Avogadro's number**, named in honor of the brilliant Italian contemporary of Dalton who recognized that the simplest molecules of compounds might very well be triatomic, tetratomic, or more complex, in con-

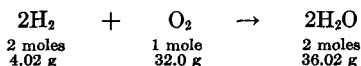
TABLE 5-1 *Mole relationships*

name	formula	weight of unit indicated by formula, awu*	weight of 1 mole, g	number and kind of particles in 1 mole*
nitrogen	$N_2$	28.0	28.0	$6.02 \times 10^{23}$ molecules
atomic nitrogen	N	14.0	14.0	$6.02 \times 10^{23}$ atoms
silver	Ag	108	108	$6.02 \times 10^{23}$ atoms
silver ions	$Ag^+$	108	108	$6.02 \times 10^{23}$ $Ag^+$ ions
methanol	$CH_3OH$	32.0	32.0	$6.02 \times 10^{23}$ molecules
sodium chloride	NaCl	58.5	58.5	$6.02 \times 10^{23}$ NaCl units, or $6.02 \times 10^{23}$ $Na^+$ ions $6.02 \times 10^{23}$ $Cl^-$ ions
barium chloride	$BaCl_2$	208	208	$6.02 \times 10^{23}$ $BaCl_2$ units, or $6.02 \times 10^{23}$ $Ba^{2+}$ ions $12.0 \times 10^{23}$ $Cl^-$ ions
ammonium sulfate	$(NH_4)_2SO_4$	114	114	$6.02 \times 10^{23}$ $(NH_4)_2SO_4$ units, or $12.0 \times 10^{23}$ $NH_4^+$ ions $6.02 \times 10^{23}$ $SO_4^{2-}$ ions

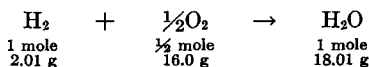
\* Weights and numbers of particles have been rounded to three significant figures.

trast to Dalton's emphasis on diatomic molecules. Avogadro's notion about the relative numbers of molecules in different gases is discussed in Chap. 8. Some of the methods for determining the Avogadro number are discussed in this text. (See Index.)

On page 104 it was stated that an equation indicates the ratio of molecules that participate in a chemical reaction. An equation may also be interpreted in terms of moles of reactants and products. For the reaction of hydrogen and oxygen to form water, the equation may be read: 2 moles of hydrogen react with 1 mole of oxygen to form 2 moles of water. And because the weights of a mole of hydrogen and of oxygen can be readily inferred from the atomic weights, the weight relationship between reactants and products can be calculated:



When an equation is being interpreted in terms of moles, the equation may be written to indicate fractions of moles. For example, the above equation may be written

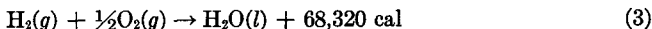
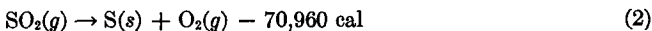
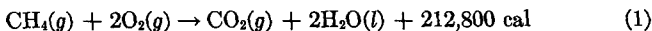


Weight relationships in chemical reactions are taken up in more detail in Chap. 9.

## ENERGY CHANGES ACCOMPANYING CHEMICAL REACTIONS

Ordinary chemical equations, such as we have been discussing, show only the substances that react and the substances that are formed. They do not show the energy changes that take place. As a rule, knowledge of the energy changes is important.

The heat given up during an exothermic chemical reaction is usually indicated in an equation, called a *thermochemical equation*, as follows. The letters in parentheses, *s*, *l*, and *g*, stand for solid, liquid, and gas, respectively.



The first two equations are read thus: (1) When 1 mole (16 g) of gaseous methane unites with 2 moles (64 g) of gaseous oxygen to form 1 mole (44 g) of gaseous carbon dioxide and 2 moles (36 g) of liquid water, 212,800 cal of heat is liberated to the surroundings. (2) When 1 mole (64 g) of gaseous sulfur dioxide is decomposed into 1 mole (32 g) of solid sulfur and 1 mole (32 g) of gaseous oxygen, 70,960 cal of heat is absorbed from the surroundings.

In discussing energy changes during chemical reactions, the chemist finds it convenient to think of each substance as having a certain heat content or **enthalpy** (Greek *enthalpein*, to warm in). The symbol for enthalpy is *H*; a heat change in a chemical reaction is termed a change in enthalpy or  $\Delta H$ . The sign  $\Delta$  means "the difference in."

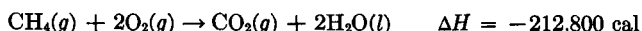
Strictly, the term "change in enthalpy" refers to the heat change during a process carried out at constant pressure. If the energy is to be precisely specified, the initial and final conditions of pressure and temperature must be known. In this text, most values for  $\Delta H$  are for processes at 25°C and 1 atm.

In reaction (1), because heat is liberated, it is evident that the heat content or enthalpy of the  $\text{CO}_2 + 2\text{H}_2\text{O}$  is not so great as that of  $\text{CH}_4 + 2\text{O}_2$ . The change in enthalpy is defined by the relation

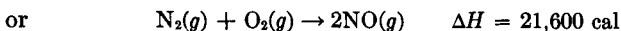
$$\Delta H = \Sigma H \text{ products} - \Sigma H \text{ reactants}$$

The sign  $\Sigma$  means "the sum of all" or "the summation of."

For an exothermic reaction  $\Delta H$  is negative, so that reaction (1) can be written

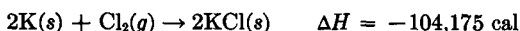


The heat energy that is transformed to chemical energy during an endothermic chemical reaction may be indicated as follows:

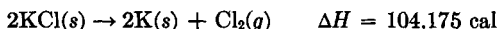


Either equation is read thus: When 1 mole (28 g) of gaseous nitrogen unites with 1 mole (32 g) of gaseous oxygen to form 2 moles (60 g) of gaseous nitric oxide, 21,600 cal of heat energy is absorbed from the surroundings.

Consider the exothermic thermochemical equation



which states that 104,175 cal is liberated when 2 moles of potassium chloride is formed. From this we would infer that the decomposition of 2 moles of potassium chloride into elemental potassium and chlorine would require the addition of 104,175 cal. This is correct. *If a given reaction is exothermic, the reverse reaction is endothermic,* and the heat absorbed in the endothermic reaction equals the heat liberated in the exothermic reaction. The thermochemical equation for the decomposition is written as follows:



Although the energy relationships for chemical changes are usually expressed in heat units (calories), the energy need not be supplied or removed as heat energy. For example, in decomposing 2 moles of KCl, the energy equivalent to 104,175 cal may be supplied as electrical energy in electrolysis.

**EXPERIMENTAL DETERMINATION OF HEAT OF REACTION.** The amount of heat change that takes place during a chemical reaction is measured in a device called a **calorimeter** (Fig. 5-3). In one common type of device, the reaction takes place in a container that is immersed in a weighed quantity of water in an insulated vessel. If the reaction is a combustion, the reaction chamber is made of heavy

A bomb-type calorimeter.

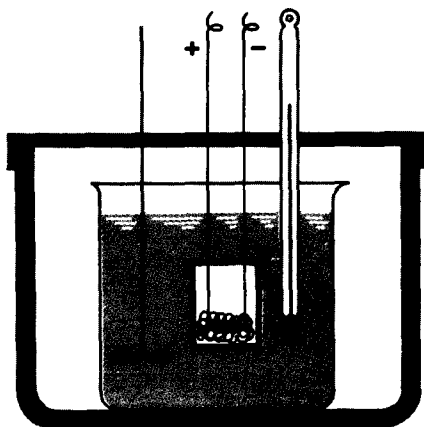


FIG. 5-3

steel to withstand the pressure generated by the gases formed during the burning. The heat given off, or absorbed, is found by placing a weighed quantity of the reactants in the container, allowing the reaction to take place, and then noting the temperature change in the surrounding water. From the weights of the materials involved (water, products of the reaction, and calorimeter), the change in their temperature, and their specific heats, the amount of heat evolved or absorbed during the reaction can be calculated.

## CLASSIFICATION OF COMPOUNDS

*Electrovalent and Covalent Compounds.* An important classification of compounds is based on the kind of bonds that hold the atoms in the compound together (Chap. 4). If all the bonds are pairs of shared electrons, the compound is said to be **covalent**. If one or more bonds are primarily due to the attraction between ions of unlike charge, the compound is said to be **electrovalent**.

*Organic and Inorganic Compounds.* One of the oldest methods of classifying compounds is based on whether the compound contains carbon as one of the combined elements. Compounds that contain carbon are called **organic compounds**; those which do not are called **inorganic compounds**.

**ORGANIC COMPOUNDS.** The organic compounds that occur in nature are found mostly in plants and animals, or in materials of plant and animal origin, such as coal, natural gas, and petroleum. Carbohydrates, fats, proteins, and alcohols represent familiar classes of organic compounds; these and other types are discussed in later chapters. Thousands of organic compounds that do not occur in nature have been synthesized in chemical laboratories. Organic compounds make up possibly 90 per cent of the number of known com-

pounds. Organic compounds are usually covalent, although many electrovalent ones exist.

**INORGANIC COMPOUNDS.** Inorganic compounds constitute rocks, clay, sand, and other earthy materials. Most of the ionic substances that we have mentioned are inorganic, for example,  $\text{Ca}(\text{OH})_2$ ,  $\text{K}_2\text{S}$ , and  $\text{Na}_2\text{SO}_4$ . Actually, a few compounds that contain carbon may be classified as inorganic rather than organic because they are earthy or rocklike and are quite similar to other mineral substances. Calcium carbonate,  $\text{CaCO}_3$ , magnesium carbonate,  $\text{MgCO}_3$ , and sodium cyanide,  $\text{NaCN}$ , are examples of such inorganic compounds.

**Electrolytes and Nonelectrolytes.** Another method of classifying compounds in two broad divisions is based on whether the molten compound or a solution of it will conduct a current of electricity. If a molten compound or its solution is a conductor of an electric current, the compound is termed an **electrolyte**; if not, the compound is a **nonelectrolyte**. The test is made quite easily. In the apparatus shown in Fig. 5-4, the electrical cord is the usual type of light cord

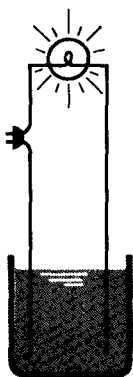


FIG. 5-4

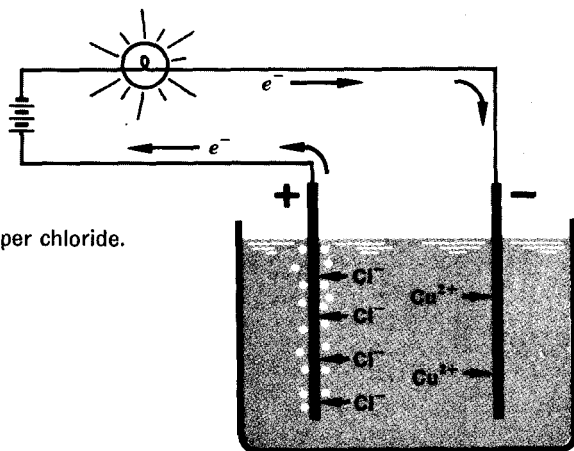
Apparatus for testing a solution for electrical conductivity.

with a socket for a light bulb and a plug for insertion into a regular 110-volt outlet. However, one of the wires is cut in two so that the current cannot flow. When the two ends of the cut wire are immersed in pure water, the light will not burn; but when they are dipped into a water solution of common salt (sodium chloride) or hydrochloric acid or sodium hydroxide, the electric current is conducted by the solution, and the light burns. Sodium chloride, hydrochloric acid, and sodium hydroxide are therefore classed as electrolytes. On the other hand, when the two ends of the cut wire are immersed in a water solution of sugar or alcohol or glycerin, the light does not burn. Sugar, alcohol, and glycerin are therefore classed as nonelectrolytes.

It is important to note at this point that all electrovalent compounds that dissolve in water make an electrolyte solution, whereas some covalent compounds that dissolve in water are electrolytes and some are not. If the pure molten substance conducts the electric current, it is an electrovalent substance.

**How CURRENT FLOWS THROUGH ELECTROLYTE.** Suppose that we arrange our "cut wire" apparatus as shown in Fig. 5-5. We shall use a direct current<sup>1</sup> from a battery of dry cells, instead of the 110-volt alternating current, and our electrolyte will be copper chloride,  $\text{CuCl}_2$ , dissolved in water. When the current is turned on, we are

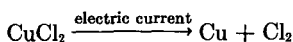
<sup>1</sup> There are two kinds of current: alternating and direct. Alternating current, the type commonly used in homes and industry for lighting, heating, and operating electric motors, etc., is produced by rotating coils of copper wire in a magnetic field. In such current, the electrons oscillate first in one direction and then in the opposite direction. In direct current, produced by batteries and by the rectification of alternating current, the electrons flow only in one direction.



Electrolysis of copper chloride.

FIG. 5-5

sure that it is flowing through the circuit because the light bulb burns. We also notice that chlorine, a greenish-yellow gas, bubbles from the solution at the positive electrode (the **anode**) and that metallic copper begins to plate out on the negative electrode (the **cathode**). When the battery is disconnected, the light goes out and the chemical changes cease. When the battery is connected again, the light begins to burn, additional copper plates out, and more chlorine bubbles appear. If the battery is left connected for a long period of time, used cells being replaced as necessary, the light dims and eventually goes out. If we now examine the water solution, we find that no copper chloride remains. It has all been changed into elemental copper, which plated out, and into elemental chlorine, which escaped as a gas:



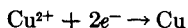
The chemical reaction that occurs when an electric current flows through an electrolyte— $\text{CuCl}_2$  in the example above—is called **electrolysis**. The process is of great importance in the production of many elements and compounds and in electroplating.

These observations naturally raise several questions:

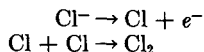
1. How did the electric current pass through the solution?
2. What caused the copper to be formed at the cathode?
3. What caused the chlorine to be formed at the anode?
4. What caused the current to stop flowing eventually, although the worn-out batteries were replaced by fresh ones?

The answers to these questions begin with our recognition of the fact that copper chloride,  $\text{CuCl}_2$ , is composed of ions. A more precise way of representing a unit quantity of copper chloride is as follows:  $\text{Cu}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Cl}^-$ . When copper chloride is dissolved in water, the ions become separated and mix with the water, every ion being free to

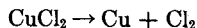
move around at random among the water molecules. When the current is turned on, there is a mass movement of  $\text{Cu}^{2+}$  ions toward the negative pole or cathode; there is also a mass movement of  $\text{Cl}^-$  ions toward the positive pole or anode. At the cathode, electrons are picked up by the copper ions. In this manner, the copper ions are changed to copper atoms:



At the anode, electrons are given up by the chloride ions. The chlorine atoms that are formed then join in pairs to make chlorine molecules:



The equation representing the overall reaction may be written this way:



We can summarize as follows:

1. A solution of an electrolyte contains ions.
2. The current (a flow of electrons) enters the solution at the cathode. The entering electrons are taken up by the positive ions (cations).
3. Electrons leave the solution at the anode. Negative ions (anions) give up these electrons.
4. When all the ions originally present have been changed to neutral particles, the current can no longer flow.

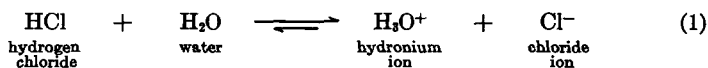
## SOURCES OF IONS

**Electrovalent Compounds.** Electrovalent compounds are composed of ions even when in the dry, solid form. It is only when such substances are melted or dissolved in a solvent that the ions are free to migrate to an anode or cathode. All electrovalent compounds are electrolytes.

It should be emphasized that in the case of electrovalent compounds such as  $\text{NaCl}$  and  $\text{CuCl}_2$ , the water plays no special part in conducting the current beyond furnishing a medium in which the ions can move about. When pure sodium chloride is melted, at about  $800^\circ\text{C}$ , this pure liquid is an excellent conductor of an electric current. X-ray studies show that sodium and chloride ions are present even in solid salt.

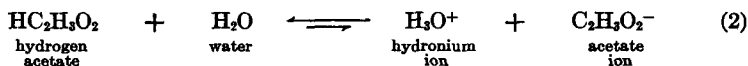
**Polar Covalent Compounds.** It will be recalled that a polar covalent molecule as a whole is an electrically neutral particle (Chap. 4). Pure liquid hydrogen chloride,  $\text{HCl}$ , pure liquid ammonia,  $\text{NH}_3$ , pure liquid hydrogen acetate,  $\text{HC}_2\text{H}_3\text{O}_2$ , and pure water,  $\text{H}_2\text{O}$ , are very poor conductors of electric current. But if we make a water solution

of hydrogen chloride and test it with our "cut wire" apparatus, we find that the light burns brilliantly; that is, the water solution of hydrogen chloride, HCl, is a conductor of electricity. On the other hand, if hydrogen chloride is dissolved in benzene, the solution does not conduct electricity. What is the reason for this difference? In order to account for the conductivity, we must assume that the covalent hydrogen chloride molecules are able to form ions in the water solution but are unable to do so in the benzene solution. Actually the ions result from a chemical reaction between hydrogen chloride molecules and water molecules, as shown in the following equation:

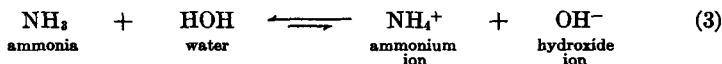


This water solution is hydrochloric acid.

Acetic acid, when dissolved in water, also forms a solution that is a conductor of electricity. Because pure acetic acid (hydrogen acetate) is a covalent compound, we assume that the ions result from a reaction similar to the one above:



Ammonia, a covalent compound, also reacts with water to produce ions:



This water solution is ammonium hydroxide and is often represented by the formula  $\text{NH}_4\text{OH}$ . Reactions (1) and (3) are shown by diagrams in Fig. 5-6.

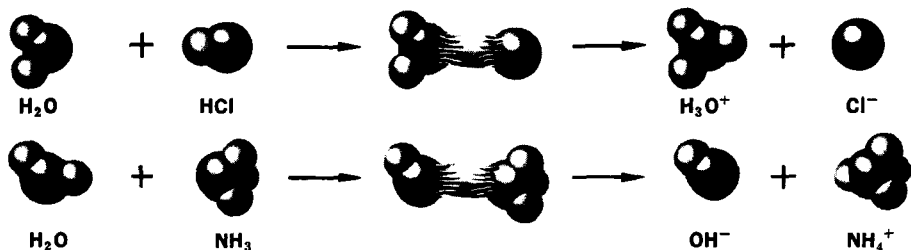


FIG. 5-6

Pure hydrogen chloride and pure ammonia are not conductors of electricity. Their water solutions are conductors because the pure substances react with water to form ions.

**CHEMICAL EQUILIBRIA.** Note that double arrows are used in Eqs. (1) to (3). As in the case with a great number of chemical reactions, the conditions required for a reaction to occur also allow the products



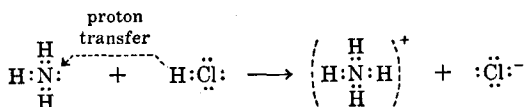
to react to form the original substances; that is, the reaction is reversible. Consider what happens when ammonia is added to water—Eq. (3). At the instant that the two are brought together, only  $\text{NH}_3$  and  $\text{H}_2\text{O}$  molecules can react, because only these two are present. A very short time later some  $\text{NH}_4^+$  and  $\text{OH}^-$  ions will have formed, and the reverse reaction starts, slowly at first, because very few of these ions are present to react. Both reactions continue to take place simultaneously. In time the concentrations of  $\text{NH}_3$ ,  $\text{HOH}$ ,  $\text{NH}_4^+$ , and  $\text{OH}^-$  become adjusted so that both reactions are occurring at the same speed. This condition is described as a **chemical equilibrium** and is shown in equations with double arrows. In an equilibrium system, the rates of the competing reactions are equal; the longer arrow used in some equations points toward the reactants whose amounts are greater at equilibrium.

The factors that determine the relative amounts of reactants and products at equilibrium are discussed in detail in Chap. 12. Let us note here that when equilibrium is reached for reaction (1), very little  $\text{HCl}$  is left in the mixture; its concentration is low, and the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{Cl}^-$  are relatively high. The opposite is true for reactions (2) and (3); in these solutions relatively few ions are formed, and the solutions are rather poor conductors of the electric current.

An interesting and important question is: Why do hydrogen chloride and other similar compounds form ions when dissolved in solvents like water but do not when dissolved in certain other solvents, such as benzene? This question can be answered in terms of the structures of the molecules involved. It was pointed out in Chap. 4 that both hydrogen chloride and water molecules are highly polar. We account for the formation of  $\text{H}_3\text{O}^+$  and  $\text{Cl}^-$  ions by noting the attraction of the oxygen side of the  $\text{H}_2\text{O}$  molecule (see Fig. 5-6) for the proton (hydrogen nucleus) of the  $\text{HCl}$  molecule; also we note the strong attraction of the chlorine atom for the electron pair of the  $\text{H}-\text{Cl}$  bond; these two effects result in the transfer of the proton to the water molecule. The additional electron left with the chlorine atom produces a negative ion ( $\text{Cl}^-$ ), and the positive proton gained by the  $\text{H}_2\text{O}$  molecule produces a positive ion ( $\text{H}_3\text{O}^+$ ).

On the other hand, when hydrogen chloride is dissolved in the nonpolar liquid benzene ( $\text{C}_6\text{H}_6$ ), protons are not pulled away from  $\text{HCl}$  molecules to form ions, because the localized negative charges in benzene molecules are not so large as in water molecules.

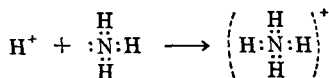
There are other liquids that behave like water. Liquid ammonia, for example, consists of polar covalent molecules, and when hydrogen chloride is added to it, ions are produced:



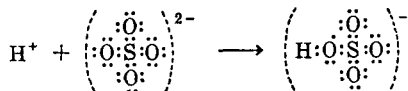
Although water is not the only solvent in which substances dissolve to form ions, it is by far the most important polar solvent. Proton transfers, such as we have been discussing, are treated in greater detail in the next section.

**Hydronium Ion.** The suffix *-onium* is frequently encountered in naming ions. In solution chemistry it is sometimes used to refer to the positive ion that results from the interaction of a molecule of solvent with a proton,  $H^+$ . In liquid ammonia,  $NH_3$ , the onium ion is  $NH_4^+$ , ammonium; and in liquid water the onium ion for many years has been written  $H_3O^+$ , hydronium.

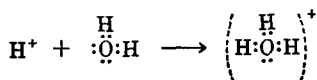
In a polar solvent any ion has a tendency to attract molecules of the solvent and become solvated; in the case of water, the solvated ions may also be called **aquated ions**. It has been known for a long time that the simple proton,  $H^+$ , does not exist as a separate particle except under unusual circumstances, such as in a vacuum discharge tube. Ordinarily,  $H^+$  is strongly attracted to a pair of electrons on a neighboring particle and is held by a covalent bond, as for:



or



In the case of water, this reaction has long been written



but, recently, attempts to show conclusively that  $H_3O^+$  is a separate ion in water solution have failed. Instead, evidence from spectro-

Schematic representation of structures of  $H_3O^+$  and  $H_9O_4^+$ .

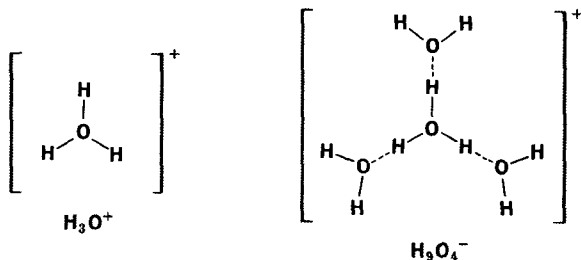
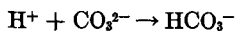


FIG. 5-7

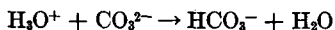
scopic studies indicates that the aquated proton is more complex, perhaps being  $H_9O_4^+$ . Diagrams of possible structures for  $H_3O^+$  and  $H_9O_4^+$  are shown in Fig. 5-7. Other evidence indicates that the hy-

droxide ion is not simply  $\text{OH}^-$  when in water solution but may be  $\text{H}_7\text{O}_4^-$ . The structures of  $\text{H}_5\text{O}_4^+$  and  $\text{H}_7\text{O}_4^-$  are probably related to the structure of liquid water, a rather complicated structure, as we shall see in Chap. 6.

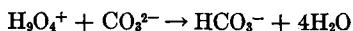
The involved mixture of facts and theories about the aquated proton has led the chemist to use a variety of symbols to represent this particle. He may wish merely to show that a proton is available for reaction in solution and writes



Or he may wish to emphasize the role of water and writes



In either case it might be more correct to write



but this is somewhat cumbersome and would be worthwhile only in special cases.

In this text we use either  $\text{H}^+$  or  $\text{H}_3\text{O}^+$  for the proton in water solution, with the understanding that other water molecules are strongly attracted to it. Sometimes it is convenient to use (*aq.*) to indicate that an ion is aquated, or held by water molecules. For example,  $\text{H}^+(\text{aq.})$ ,  $\text{Cu}^{2+}(\text{aq.})$ ,  $\text{OH}^-(\text{aq.})$ , or  $\text{Mg}^{2+}(\text{aq.})$ . Generally, an ion is more strongly aquated the higher its charge and the smaller its size.

**Strong and Weak Electrolytes.** It is a fact that water solutions of sodium chloride and other electrovalent compounds as well as water solutions of certain covalent compounds are excellent conductors of electricity. Such compounds are said to be *strong electrolytes*. Strong electrolytes exist in solution completely or almost completely in the form of ions.

On the other hand, water solutions of many covalent compounds are poor conductors of electricity. Water solutions of ammonia (ammonium hydroxide) and of hydrogen acetate (acetic acid) are examples. Such compounds are said to be *weak electrolytes*. We assume in these cases that only a small percentage of the dissolved molecules have reacted with water to form ions. The great bulk of the dissolved substance is present as covalent molecules.

Actually, the terms strong and weak electrolytes cannot be considered clear-cut classifications, for strong electrolytes may be weakly strong, moderately strong, strong, very strong, etc., and weak electrolytes may be subclassified in the same manner. That is, there are all degrees of weak and strong, so that the dividing line between the two is not always clear. This topic is discussed in greater detail in the chapter on ionic equilibrium.

In addition to being classified as to strength, electrolytes may be classified as to type. The three common types to be considered in

this chapter are *acids*, *bases*, and *salts*. There are many examples of strong and weak electrolytes in the first two classes, but practically all salts are strong electrolytes.

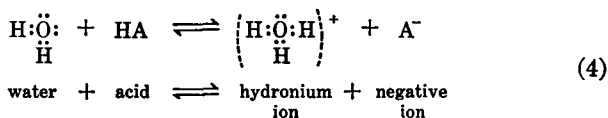
## ACIDS AND BASES

Acids and bases were defined by chemists centuries ago in terms of the properties of their water solutions. In these terms, an acid is a substance whose water solution has a sour taste, turns blue litmus red, reacts with active metals to form hydrogen, and neutralizes bases. Following a similar pattern, a base is defined as a substance whose water solution has a bitter taste, turns red litmus blue, feels soapy, and neutralizes acids.

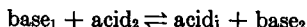
Some common examples of acids and bases include the following. *Acids*: hydrochloric (HCl), nitric (HNO<sub>3</sub>), sulfuric (H<sub>2</sub>SO<sub>4</sub>), and acetic (HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>); *bases*: sodium hydroxide (NaOH), potassium hydroxide (KOH), calcium hydroxide (Ca(OH)<sub>2</sub>), and ammonium hydroxide (NH<sub>4</sub>OH). The first three in each group are highly or completely ionized in water solutions. These are classed as *strong acids* or *strong bases*, respectively. Acetic acid and ammonium hydroxide are sparingly ionized in water solutions and are accordingly classed as a *weak acid* and a *weak base*, respectively.

Although the definition of acids and bases in terms of properties of their water solutions is of practical value, it greatly limits the scope of this field of chemistry. In 1923, J. N. Brønsted (Denmark) and J. M. Lowry (England) independently suggested that acids be defined as **proton donors** and bases as **proton acceptors**. By this definition, a great variety of closely related chemical properties and chemical reactions can be correlated. In this chapter we are chiefly concerned with some of the more common acid-base relationships as they apply to water systems; in Chap. 13 other aspects of the Brønsted-Lowry theories are taken up.

**Proton Transfer.** Let us consider from the Brønsted point of view what the proton-donating species is in water solutions of acids like HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>. If we use the symbol HA for the dissolved proton donor, then A<sup>-</sup> represents the negative ion, for example, Cl<sup>-</sup> or HSO<sub>4</sub><sup>-</sup>, and we can write



or we can describe the reaction as

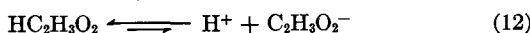
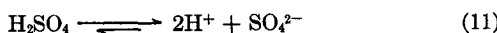
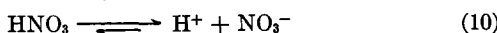
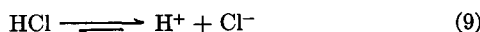
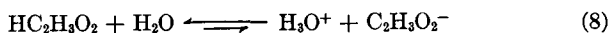
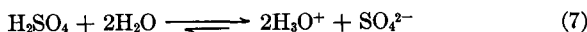
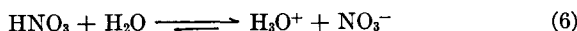
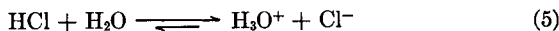


The latter description focuses attention on two useful concepts. First,

**FORMULAS AND EQUATIONS;  
CLASSES OF COMPOUNDS**

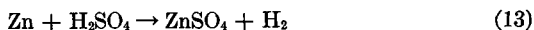
for every acid or proton donor, for example, HA, there must be a base or proton acceptor, for example, H<sub>2</sub>O. Second, as is clear from the reverse reaction, when base<sub>1</sub> and acid<sub>1</sub> react, another potential acid and potential base are formed.

In water solutions of acids the strong proton donor present is the aquated proton, H<sup>+</sup>(aq.), which we write as either H<sub>3</sub>O<sup>+</sup> or simply H<sup>+</sup>. Equations (5) to (8) are specific illustrations of Eq. (4); Eqs. (9) to (12) show the same reactions in the simplified form with water omitted:

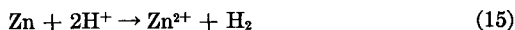
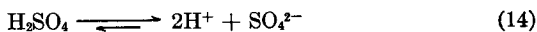


In referring to changes such as those shown by Eqs. (4) to (12), it is customary to say that the acids have *ionized*. It is apparent that the actual acid in water solutions of HCl, H<sub>2</sub>SO<sub>4</sub>, etc., is the hydronium ion (H<sub>3</sub>O<sup>+</sup> or some species of this ion). The properties that are common to aqueous acid solutions (sour taste, color changes of indicators, etc.) are thought to be due to this ion. A particular acid solution has additional properties due to the other ionic or molecular species present. For example, HCl and H<sub>2</sub>SO<sub>4</sub> solutions differ in certain properties, owing to the presence of Cl<sup>-</sup> ions in one solution and SO<sub>4</sub><sup>2-</sup> ions in the other.

In writing equations for the reaction of aqueous acid solutions with different substances, we often write an equation that shows only the overall change. For example, if we take concentrated H<sub>2</sub>SO<sub>4</sub>, add water, and drop in a small piece of zinc, the zinc dissolves, and hydrogen gas bubbles out of the solution. A simple equation can be written to represent this change:



A more complete representation is



Note that Eqs. (14) and (15) can be added and the H<sup>+</sup> ions cancelled to give an equation similar to (13):



If hydrochloric or acetic acid were used instead of sulfuric, the reaction to liberate hydrogen gas would be the same, that is, just as written in Eq. (15).

**Naming Acids.** For water solutions of binary acids, the name is built around the name of the element other than hydrogen, with the prefix *hydro-* and the suffix *-ic*. Examples:

	acid name	name of pure compound
HCl	hydrochloric acid	hydrogen chloride
HBr	hydrobromic acid	hydrogen bromide
H <sub>2</sub> S	hydrosulfuric acid	hydrogen sulfide

For one type of ternary acid, the name shows the element other than oxygen or hydrogen and ends in *-ic*. Examples:

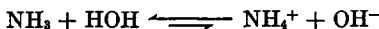
	acid name	name of pure compound
H <sub>2</sub> SO <sub>4</sub>	sulfuric acid	hydrogen sulfate
HNO <sub>3</sub>	nitric acid	hydrogen nitrate
H <sub>3</sub> PO <sub>4</sub>	phosphoric acid	hydrogen phosphate

Names of a second type of ternary acid end in *-ous*. Examples:

	acid name	name of pure compound
H <sub>2</sub> SO <sub>3</sub>	sulfurous acid	hydrogen sulfite
HNO <sub>2</sub>	nitrous acid	hydrogen nitrite
H <sub>3</sub> PO <sub>3</sub>	phosphorous acid	hydrogen phosphite

Methods of naming other types of ternary acids are introduced in later chapters.<sup>1</sup>

**Properties of Bases.** The properties that characterize water solutions of common bases (bitter taste, action with litmus and acids, etc.) are due to the hydroxide (OH<sup>-</sup>) ion, a powerful Brønsted base. The hydroxides of the IA and IIA elements are ionic compounds; hence, water solutions of these hydroxides, for example, NaOH, KOH, Ca(OH)<sub>2</sub>, and Ba(OH)<sub>2</sub>, are strong bases and have high concentrations of hydroxide ions. Ammonium hydroxide, formed by dissolving ammonia (NH<sub>3</sub>) in water, is a weak base. In an equilibrium mixture, covalent molecules of ammonia and water are present abundantly, and NH<sub>4</sub><sup>+</sup> and OH<sup>-</sup> ions are present in relatively small amounts:



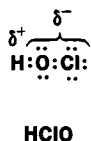
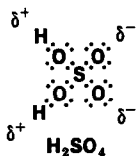
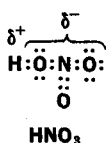
The pungent odor of ammonium hydroxide is due to some gaseous ammonia coming out of solution.

## STRUCTURES OF HYDROXY COMPOUNDS

Ordinary formulas for oxygen-containing acids, such as HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, or HClO<sub>4</sub>, do not reveal an interesting feature of the structures of these molecules. In all acids of this type, the hydrogen is covalently bonded to the oxygen. Structural formulas like those in Fig. 5-8 show that OH groups are present in these acids.

<sup>1</sup> Practices in naming pure compounds and water solutions are not uniform. Pure H<sub>2</sub>SO<sub>4</sub>, hydrogen sulfate, is often referred to as sulfuric acid; and a water solution of H<sub>2</sub>S, hydrosulfuric acid, is often referred to as hydrogen sulfide (solution).

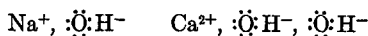
FORMULAS AND EQUATIONS;  
CLASSES OF COMPOUNDS



Polar —OH groups are present in oxy acids.

FIG. 5-8

The question arises: Why does one OH-containing ternary compound, such as HOCl, act as an acid and another, such as NaOH, as a base? One explanation is based on the differences in electronegativities of the elements attached to the OH groups. If the element has a low electronegativity, it has little attraction for a pair of electrons, and the compound is ionic. The hydroxides of the IA and IIA families are ionic compounds:

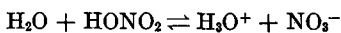


The hydroxide ion, a strong proton acceptor, is set free when these ionic hydroxides dissolve in water solution.

If the element attached to the OH group has a high electronegativity, it has a strong attraction for a pair of electrons. In combination with OH such an element forms a polar covalent compound in which the partial positive charge is associated with the hydrogen. Such compounds are formed by nonmetals, as shown in Fig. 5-8. These compounds can act as proton donors.

Also, metals other than those with the lowest electronegativities may form acidic hydroxy compounds, especially if the metal has a high oxidation number. Compounds such as  $\text{H}_2\text{CrO}_4$ , chromic acid, or  $\text{HMnO}_4$ , permanganic acid, are strong acids in water solution. With their moderate electronegativities and very high positive oxidation states, the chromium and manganese in these two compounds attract electrons so strongly that the hydrogens are left with considerable  $\delta^+$  character.

For OH compounds that act as proton donors toward water, such reactions as these can be written:



Ions like  $\text{NO}_3^-$ ,  $\text{ClO}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{MnO}_4^-$  are called *oxy-ions*; the formula for the ion alone commonly shows the oxygen second.

We may state a general rule to describe the types of compounds just discussed. Hydroxy compounds of metals with low electronegativities yield the strong base  $\text{OH}^-$ , whereas hydroxy compounds of nonmetals, or metals of high electronegativity and high oxidation number, tend to act as acids.

The hydroxy compounds of carbon present an interesting and somewhat different picture. In group IV and with an electronegativ-

ity of 2.5, carbon has neither a pronounced tendency to gain or lose electrons in reacting with other elements. A simple hydroxide of carbon, ethyl alcohol, for example, has only a slight tendency to act as an acid (it also has a slight tendency to act as a base); acetic acid, a hydroxy compound of carbon that has an additional oxygen bonded to the carbon, is an acid. Evidently the attraction of the second oxygen for electrons gives rise to a more polar bond between the oxygen and hydrogen of the OH group, as shown in Fig. 5-9.

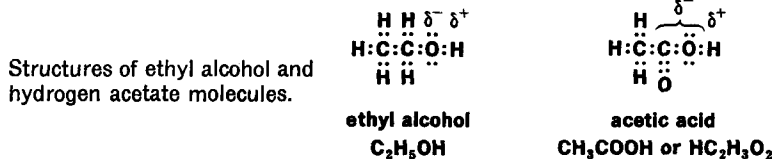
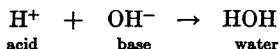


FIG. 5-9

## NEUTRALIZATION

When acids and bases are brought together in a water solution, the hydrogen ions of the acid and the hydroxide ions of the base combine to form water. The equation is



This is the fundamental reaction that occurs when acids and bases neutralize each other in water solutions. The characteristic properties of both acid and base disappear when the ions responsible for these properties react to form water.

## SALTS

Ionic compounds are commonly called salts. Some examples are

$\text{NaCl}$ or $\text{Na}^+$ , $\text{Cl}^-$	sodium chloride
$\text{KCl}$ or $\text{K}^+$ , $\text{Cl}^-$	potassium chloride
$\text{Ca}(\text{NO}_3)_2$ or $\text{Ca}^{2+}$ , $\text{NO}_3^-$ , $\text{NO}_3^-$	calcium nitrate
$\text{Na}_2\text{SO}_4$ or $\text{Na}^+$ , $\text{Na}^+$ , $\text{SO}_4^{2-}$	sodium sulfate

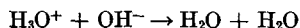
Because salts are electrovalent compounds, they exist in water solutions entirely as ions. Strictly speaking, ionic compounds such as  $\text{NaOH}$  and  $\text{Ca}(\text{OH})_2$  are salts. Because the anion  $\text{OH}^-$  is a very strong base, they are perhaps more often called bases to emphasize this property. We shall see in Chap. 13 that the anions in all common salts, for example,  $\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$ , can be proton acceptors and are therefore bases.

**Salt Formation During Neutralization.** The formation of a salt solution in conjunction with an acid-base reaction is an important type of reaction. In terms of the Brønsted-Lowry definitions, the

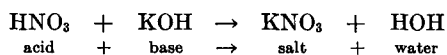


FORMULAS AND EQUATIONS;  
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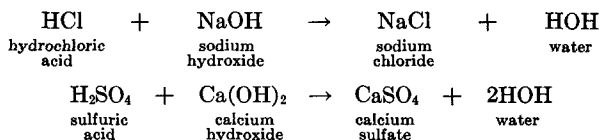
neutralization reaction in the case of water solutions of HCl and NaOH can be described as



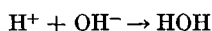
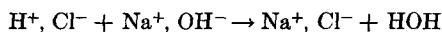
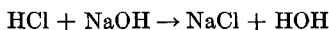
After this reaction is complete, there remains a solution of  $\text{Na}^+$  and  $\text{Cl}^-$  ions. Although these two ions are not involved in the neutralization, we can say that the NaCl solution is formed as a result of the acid-base reaction. An older representation of the neutralization reaction simply shows the initial acid and base that are brought together and what substances are present when the reaction is over, without regard to the solvents used, if any. The reaction between  $\text{HNO}_3$  and KOH, either in the pure form or in water solution, was interpreted as



Overall neutralization equations are still commonly written in this fashion. Other examples are:



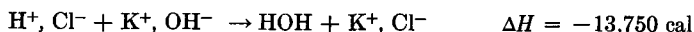
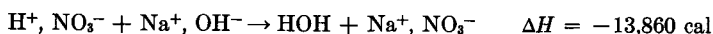
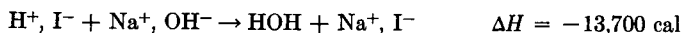
Each of the following four equations may be used to represent the neutralization of hydrochloric acid and sodium hydroxide in water solutions:



The first equation merely shows what substances are brought together and what substances are present when the reaction is completed. The second, in addition to showing this, indicates that hydrochloric acid, sodium hydroxide, and sodium chloride are composed of ions and that water is made up of covalent molecules. The last two equations are ionic equations and show as reactants or products only those particles which took part in the *chemical reaction*. These two emphasize that the  $\text{Na}^+$  ion and the  $\text{Cl}^-$  ion are merely "spectator ions," which do not change chemically in any way. The third equation is a satisfactory way of emphasizing the donation and acceptance of the proton, but because the hydronium ion may be  $\text{H}_3\text{O}^+$  or something else, the fourth equation may be just as satisfactory.

Evidence that the reaction between  $\text{H}^+$  and  $\text{OH}^-$  ions is the only chemical reaction occurring during neutralization of strong acids and bases is obtained by measuring the amount of heat given off during neutralization. If we mix equivalent quantities of any strong acid

and any strong base and measure the heat given off, we find that the same amount of heat is evolved, no matter what strong acid or strong base is used. About 13,700 cal is evolved for each mole (18 g) of water formed. Below are the equations for four apparently different neutralizations with an indication of the amount of heat evolved per mole of water formed:



Because virtually the same amount of heat is evolved in each case, we assume that the same reaction has occurred, although we are using different substances. If we omit the "spectator ions" from each of these four equations, each is simplified to



where  $\simeq$  means "is approximately equal to."

On the other hand, if we measure the heat evolved per mole of water produced when a weak acid or a weak base is neutralized, we find that the amount of heat varies, depending on what acid or base is used. Here two reactions are taking place: (1) the union of  $\text{H}^+$  ions with  $\text{OH}^-$  ions to form water and (2) the reaction of covalent molecules with water to produce more ions.

## CHAPTER REVIEW

### Terms

Formula, valence number, oxidation number, polyatomic ion, binary compound, *-ide*, ternary compound, *-ate*, chemical equation, mole, molar weight, Avogadro's number, enthalpy, thermochemical equation, heat of reaction, calorimeter, electrovalent, covalent, organic, inorganic, electrolyte, non-electrolyte, anode, cathode, anion, cation, electrolysis, reversible reaction, chemical equilibrium, *-onium*, solvated, aquated, strong electrolyte, weak electrolyte, acid, base, salt, proton donor, proton acceptor, Brønsted-Lowry definition, strength of acids and bases, proton transfer, ionize, *hydro—ic*, *-ous*, *-ite*, *-ic*, neutralization, spectator ion, heat of neutralization.

### Exercises

1. Why can the oxidation numbers of A-family members be predicted with greater reliability than those of B-family members?
2. Using the periodic table, propose a likely oxidation number for the first-named element in each of the following compounds: cesium nitrate, antimony chloride, strontium carbonate, hydrogen astatide, hydrogen telluride, indium chloride.

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3. Based on the rules stated in this chapter, assign oxidation numbers to each of the elements in the following compounds:  $\text{RbClO}_3$ ,  $\text{AuCl}_3$ ,  $\text{SnO}_2$ ,  $\text{NaNO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{BrCl}$ ,  $\text{CaH}_2$ ,  $\text{Na}_2\text{O}_2$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{Ca}(\text{ClO})_2$ ,  $(\text{NH}_4)_2\text{SO}_4$ .
4. Name the following compounds, using the *-ide* convention:  $\text{Na}_2\text{O}$ ,  $\text{SnCl}_2$ ,  $\text{SnCl}_4$ ,  $\text{NH}_4\text{Br}$ ,  $\text{KOH}$ ,  $\text{PbI}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CaH}_2$ ,  $\text{ZnS}$ .
5. Name the following compounds, using the *-ate* and *-ite* conventions:  $\text{FeSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{BaCO}_3$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{Ba}(\text{ClO}_3)_2$ ,  $(\text{NH}_4)_3\text{PO}_4$ ,  $\text{Ba}(\text{ClO}_2)_2$ ,  $\text{CsNO}_2$ ,  $\text{SrSO}_3$ .
6. Write the formula for each of the following compounds, using the periodic table as a guide when needed: zinc carbonate, ammonium sulfate, iron(III) nitrate, sodium phosphate, potassium oxide, copper(I) bromide, magnesium nitride, hydrogen fluoride, aluminum hydroxide, gallium chloride, sodium selenide, calcium sulfite, potassium nitrite.
7. Balance the following equations:
  - a.  $\text{Ca} + \text{N}_2 \rightarrow \text{Ca}_3\text{N}_2$
  - b.  $\text{C}_6\text{H}_{14} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
  - c.  $\text{NH}_4\text{NO}_2 \rightarrow \text{H}_2\text{O} + \text{N}_2$
  - d.  $\text{Al} + \text{Br}_2 \rightarrow \text{AlBr}_3$
  - e.  $\text{Cs} + \text{HOH} \rightarrow \text{CsOH} + \text{H}_2$
  - f.  $\text{SnCl}_4 + (\text{NH}_4)_3\text{PO}_4 \rightarrow \text{Sn}_3(\text{PO}_4)_4 + \text{NH}_4\text{Cl}$
8. Write balanced equations for the following reactions:
  - a. iron + chlorine  $\rightarrow$  iron(III) chloride
  - b. zinc nitrate + hydrogen sulfide  $\rightarrow$  zinc sulfide + \_\_\_\_\_
  - c. barium hydroxide + calcium sulfate  $\rightarrow$  \_\_\_\_\_ + \_\_\_\_\_
  - d. hydrogen + bromine  $\rightarrow$  \_\_\_\_\_
9. Water solutions of calcium chloride and ammonium carbonate, when mixed, form insoluble calcium carbonate:
$$\text{CaCl}_2 + (\text{NH}_4)_2\text{CO}_3 \rightarrow \text{CaCO}_3\downarrow + 2\text{NH}_4\text{Cl}$$
Suppose you wish to prepare some calcium carbonate by this method, but you find that, although many other water-soluble calcium and carbonate salts are available, both calcium chloride and ammonium carbonate are unavailable. Show, with equations, five substitutions that you might make. (See Table 4 of Appendix for water solubilities.)
10. What are the advantages and disadvantages of representing a chemical reaction of the type discussed in Exercise 9 with an ionic equation instead of one that shows formulas of specific compounds?
11. In each case below, an insoluble precipitate is formed when the ions are brought together in a solution. Complete and balance the ionic equation:
  - a.  $\text{Pb}^{2+} + \text{Br}^- \rightarrow$
  - b.  $\text{Sr}^{2+} + \text{SO}_4^{2-} \rightarrow$
  - c.  $\text{Bi}^{3+} + \text{S}^{2-} \rightarrow$
  - d.  $\text{Fe}^{3+} + \text{OH}^- \rightarrow$
  - e.  $\text{Ca}^{2+} + \text{PO}_4^{3-} \rightarrow$
12. Calculate the weight of 1 mole of each of the following: copper(II) chloride, glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ), chlorine molecules, chlorine atoms,  $\text{Cl}^-$  ions,  $\text{Cu}^{2+}$  ions, sulfate ions.

13. Calculate the number of:
  - a. Molecules in 10 g of ozone,  $O_3$
  - b. Atoms in 1.0 g of platinum, Pt
  - c. Bromide ions in 10 g of  $CaBr_2$
14. Calculate the weight of chlorine needed to react with 1 mole of each of the following:  $H_2$ , Na, Al.
15. Calculate the change in enthalpy when 1.0 g of sulfur, initially at  $25^\circ C$ , is burned in oxygen, initially at  $25^\circ C$ , to sulfur dioxide, and the sulfur dioxide is cooled to  $25^\circ C$ :
 
$$S(s) + O_2(g) \rightarrow SO_2(g) \quad \Delta H = -70,960 \text{ cal}$$
16. In the steel chamber of a calorimeter was placed 0.100 g of magnesium ribbon. The chamber was then filled with oxygen. After the calorimeter was filled with 1,001 g of water at  $25.00^\circ C$ , the magnesium was ignited. The temperature of the water rose to  $25.50^\circ C$ . Calculate the heat of combustion of magnesium in calories per mole. Additional data: The steel chamber weighed 151 g; specific heat of steel is  $0.11 \text{ cal}/(g \times \text{deg } C)$ . The small amount of heat retained by the combustion product, excess oxygen, and the outside container may be ignored.
17. A water solution of HCl is a good conductor of electricity; a benzene solution is not. Account for the different behavior of HCl in the two solutions.
18. Show, with equations, the electron change at the anode, the electron change at the cathode, and the overall change that occurs when each of the following is subjected to electrolysis:
  - a. A water solution of  $AuCl_3$
  - b. Molten  $MgCl_2$
  - c.  $Al_2O_3$  (dissolved in a molten medium)
19. Explain how a current of electricity is conducted through a water solution of HCl.
20. Give several examples of covalent compounds whose water solutions are conductors of electricity and several examples whose water solutions are not. In general, how do the molecular structures of the two classes differ?
21. The water solution of hydrobromic acid, HBr, is a much better conductor than that of hydrosulfuric acid,  $H_2S$ . What can be said about the composition at equilibrium of each of these solutions?
22. Which, if any, of the following compounds would probably be strong electrolytes: KCl,  $H_2O$ ,  $H_2S$ ,  $CaCl_2$ ,  $NH_3$ ,  $CH_4$ ,  $Mg(NO_3)_2$ , HI,  $CH_3OH$  (methyl alcohol),  $C_{12}H_{22}O_{11}$  (sugar)?
23. Water solutions of HCl, HBr,  $H_2SO_4$ , and  $HNO_3$  have several identical properties. Why? Name four properties characteristic of any one of these solutions.
24. The symbol  $H^+$  may be used to represent a certain particle in a cathode-ray tube, or it may be used to represent a particle in a water solution. When so used, does  $H^+$  refer to the same particle? Explain.
25. Name the following compounds as acids: HBr,  $H_2Se$ ,  $HClO_3$ ,  $HClO_2$ ,  $HBrO_3$ ,  $H_2SeO_3$ ,  $H_2SeO_4$ .

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26. Ionic compounds such as KOH, NaCl,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{OH})_2$ , and  $\text{K}_2\text{CO}_3$  are properly referred to as salts. However, it is more common to classify some of these as bases. Which ones? Would the basic properties of KOH and  $\text{K}_2\text{CO}_3$  probably be associated with the cation or the anion? Explain.
27. Cesium hydroxide ( $\text{CsOH}$ ) is a strong base, and bromine hydroxide ( $\text{BrOH}$ , more commonly written  $\text{HBrO}$ ) is an acid. Account for these differences in terms of the structures of their molecules.
28. What evidence supports the theory that the same chemical reaction occurs when water solutions of different strong acids are added to water solutions of different strong bases? What is this reaction?
29. A water solution of HX has a sour taste and turns blue litmus red. When neutralized with NaOH,  $\Delta H = -8000$  cal/mole. What conclusions about HX may be inferred from these data?
30. A water solution containing 1 mole of hydrogen fluoride, HF, per liter is 2 per cent ionized. Calculate the number of hydronium ions in 1 liter of the solution. What is the number of  $\text{F}^-$  ions? If we assume that the un-ionized hydrogen fluoride is in the form of simple HF molecules, what is the number of these particles? Instead, if we assume that the un-ionized hydrogen fluoride is present as more complex particles, having the composition  $\text{H}_2\text{F}_2$ , what is the number of these particles?

**SUPPLEMENTARY READING**

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- Szabadvary, F. (trans. R. E. Oesper): "The Birth of Stoichiometry," *J. Chem. Educ.*, **39**: 267 (1962).
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# OXYGEN, HYDROGEN, AND WATER



## Introduction.

The discovery of the elements hydrogen and oxygen and their relationship to the compound water occurred toward the end of the eighteenth century, from about 1765 to 1783. These discoveries were closely associated with the study of combustion reactions and with the overthrow of the phlogiston theory of burning.

In terms of the phlogiston theory a combustible substance contained the mysterious material *phlogiston* plus some *calyx*. When a substance burned, the phlogiston escaped into the air, leaving the calyx behind as ashes. According to this theory, when a candle burned in a closed container, the air in the container finally became saturated with phlogiston; the candle ceased burning because the air could accept no more phlogiston.

Priestley's preparations of oxygen. He frequently improvised his apparatus from household articles, using tall beer glasses for the collection of gases over mercury or water, and even a gun barrel for heating solids in his fireplace.

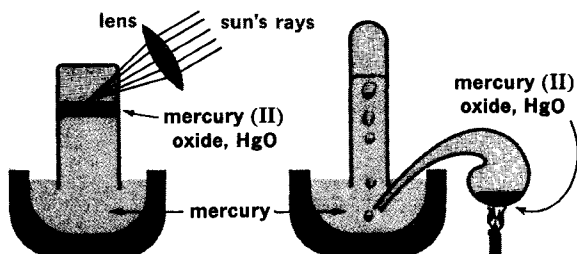


FIG. 6-1

Joseph Priestley, an English clergyman and scientist, in 1774 prepared a gas (Fig. 6-1) in which things burned more readily than in air. A candle flamed up more brightly and burned for a longer time

in this new gas than in ordinary air. Priestley supposed his new gas, which he prepared by heating mercury(II) oxide, to be like ordinary air except that it contained no phlogiston to retard the burning of the candle. Hence, he called the gas "dephlogisticated air."

In 1766, a fellow countryman of Priestley, Sir Henry Cavendish, had found that inflammable air could be prepared by the action of metals, such as iron, zinc, or tin, and dilute acid solutions. When this combustible gas was burned in air or in Priestley's gas, water was formed. It appeared that the combustible gas might be water combined with phlogiston. As a result of many experiments, Cavendish and others came to the conclusion that Priestley's gas might not be dephlogisticated air, but dephlogisticated water:

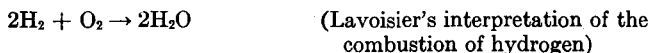
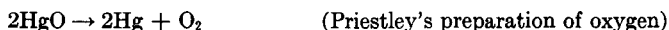
$$\begin{array}{rcl} \text{inflammable air} & = & \text{water} + \text{phlogiston} \\ \text{dephlogisticated air} & = & \text{water} - \text{phlogiston} \\ \hline \text{inflammable air} + \text{dephlogisticated air} & = & \text{water} \end{array}$$

that is,



The question as to whether Priestley's gas was dephlogisticated air or dephlogisticated water was settled in dramatic fashion by the great French theoretician, Antoine Lavoisier. Discarding the idea of phlogiston entirely, Lavoisier showed that, when a substance burns, the products weigh more than that which burned (see Fig. 1-5). From such observations he concluded that a part of the air is used in the chemical reaction. This part of the air Lavoisier called *oxygen*, meaning "acid former," and he recognized that Priestley's gas was simply a pure form of oxygen.<sup>1</sup> Lavoisier also concluded that Cavendish's combustible gas was a new element that combined with oxygen during combustion to form water. He named this element *hydrogen*, from the Greek meaning "water former."

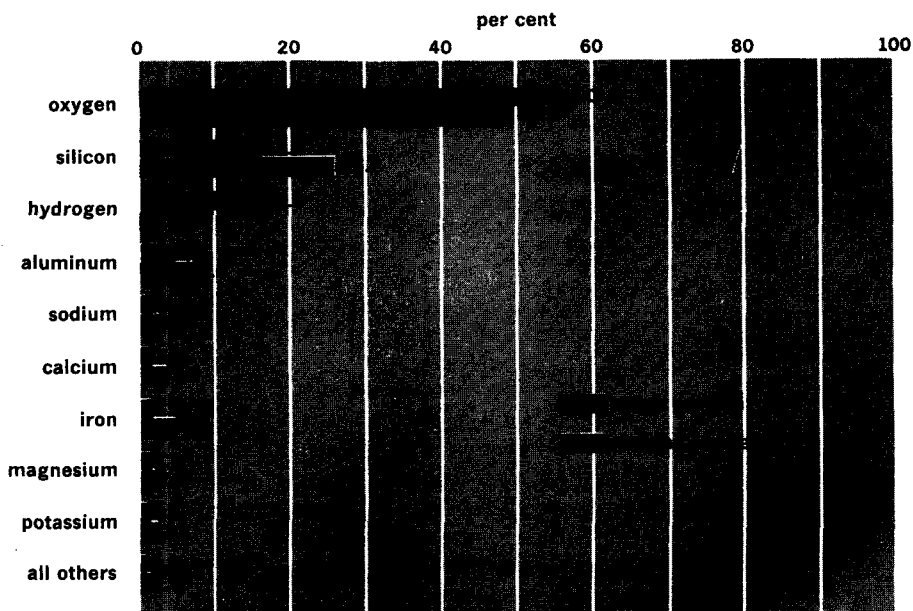
Today, we can summarize this work of Priestley, Cavendish, and Lavoisier with equations as follows:



## OCCURRENCE

Oxygen and hydrogen rank first and ninth, respectively, in abundance by weight in the earth's crust (see Fig. 6-2). Both occur abundantly in compounds (Table 6-1), but only oxygen occurs appreciably in the elemental form. It is present in air to the extent of about 21 per cent by volume. However, if we consider the universe as a whole,

<sup>1</sup> Lavoisier's idea that all acids contain oxygen was soon outmoded.



The relative abundance of elements. Elements occur in nature mainly in the form of compounds.

FIG. 6-2

hydrogen is by far the most abundant of all elements. For example, it comprises about 75 per cent of the sun.

### Natural compounds of oxygen and hydrogen

TABLE 6-1

compounds containing both	compounds containing only one
water, $H_2O$	oxygen:
sugars, $C_6H_{12}O_6$ , $C_{12}H_{22}O_{11}$	limestone or marble, $CaCO_3$
starch and cellulose, $(C_6H_{10}O_5)_x$	sand or quartz, $SiO_2$
fats	many silicate minerals
proteins	hydrogen:
clays and certain other minerals	natural gas, $CH_4$ , $C_2H_6$ , . . .
	gasoline, $C_6H_{14}$ , $C_7H_{16}$ , . . .
	other petroleum products
	natural rubber

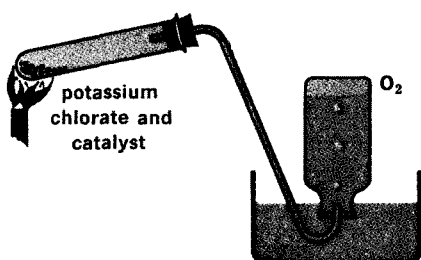
### LABORATORY PREPARATION

Methods employed by industry for the large-scale manufacture of a substance from cheap raw materials are frequently unsuitable for the laboratory because of the cost of the elaborate equipment that may be required for the process. Conversely, methods used in the



## OXYGEN, HYDROGEN, AND WATER

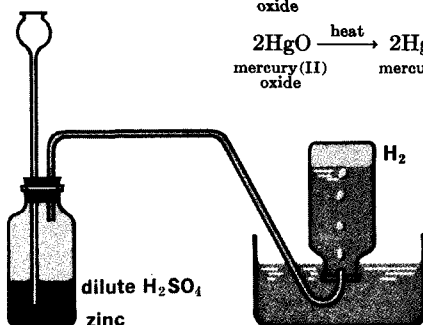
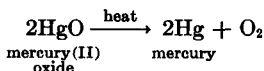
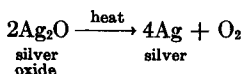
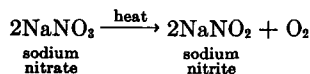
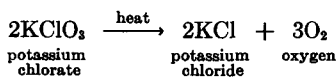
laboratory for the preparation of small quantities of a substance may call for relatively expensive chemicals in simple, inexpensive equipment.



Laboratory preparation of oxygen.

FIG. 6-3

**Oxygen.** Oxygen is commonly prepared by the *pyrolysis* (decomposition by heating) of unstable oxygen compounds. Potassium chlorate is perhaps most often used for the pyrolytic reaction, although other oxychlorine compounds may serve as well. Also, nitrates and oxides of noble metals may be used. The following equations illustrate the types of reactions:



Laboratory preparation of hydrogen.

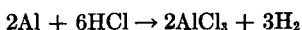
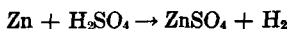
FIG. 6-4

Potassium chlorate, a white crystalline solid, decomposes into potassium chloride and oxygen when heated to a temperature slightly higher than its melting point, 368°C. Because oxygen is not appreciably soluble in water, it may be collected over water, as shown in Fig. 6-3. Although the decomposition is exothermic, the reaction tends to go slowly, once the decomposition temperature is reached. The rate of decomposition is greatly increased if either iron(III) oxide or

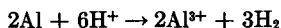
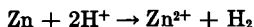
manganese dioxide is well mixed with the potassium chlorate before heating. However, the total amount of oxygen obtainable from a given weight of potassium chlorate remains the same. Neither the manganese dioxide nor the iron(III) oxide decomposes unless the temperature is excessively high; indeed, each can be recovered unchanged after the reaction is over. Such substances are called catalysts. A catalyst is a substance that influences the speed of a chemical reaction without itself undergoing a permanent chemical change. Many of the commercial products that contribute so heavily to our present standard of living could not be produced without the use of catalysts. Moreover, many of the chemical changes that occur in the life process of plants and animals are controlled by catalysts.

Oxygen may also be obtained from peroxides (see page 151).

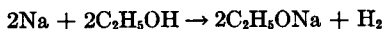
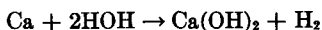
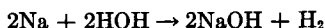
**Hydrogen.** Hydrogen is usually prepared in the laboratory by the action of acids with moderately active metals (Fig. 6-4). Dilute sulfuric and hydrochloric acids serve nicely as the acids, and metals such as zinc, aluminum, iron, and magnesium may be used as the metals. Very active metals, for example, sodium and potassium, react violently with strong acids; it is not safe to use them for preparing hydrogen. Inactive metals such as copper, silver, gold, and platinum do not react with acids to produce hydrogen. The following equations represent the type of chemical change that occurs with active metals:



or



Very active metals release hydrogen from water or alcohols, as indicated by the equations below:



ethyl  
alcohol

sodium  
ethoxide

The reaction with water is so violent that it is difficult to control. However, the reaction with alcohols is less violent and is sometimes used in synthetic organic chemistry when it is desirable to prepare the hydrogen in contact with a reactant.

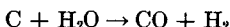
## COMMERCIAL PREPARATION

**Oxygen.** The atmosphere, which is 21 per cent oxygen by volume, is the primary source of commercial oxygen. The problem is to get the oxygen separated from the other gases present. This is accom-

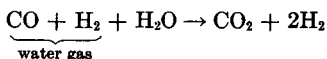
plished most efficiently by first liquefying the air and then distilling this liquid. Argon (boiling point,  $-186^{\circ}$ ) and nitrogen (boiling point,  $-196^{\circ}$ ) tend to distill off first, because they have lower boiling points than oxygen (boiling point,  $-183^{\circ}$ ). No chemical reaction is involved in this process of obtaining oxygen from air. The relatively pure oxygen is then stored as a gas in steel cylinders under pressure as high as 2,000 psi. A cylinder of oxygen contains a fairly large weight of oxygen, because the molecules are crowded close together.

In a modern air-separation plant where oxygen and nitrogen are being produced at a rate of several tons a day, the operations by which the air is liquefied and then distilled are carefully coordinated as a single process in order to conserve energy and thereby keep the cost low. That is, liquefaction and distillation proceed simultaneously, the equipment being arranged so as to permit the transfer of heat in the lines where liquefaction occurs to the columns where distillation takes place. Heavy users of oxygen—the steel industry, for example—have air-separation plants on their premises, and the armed services have mobile units that produce liquid oxygen in the field for the propulsion of missiles and rockets.

**Hydrogen. WATER GAS METHOD.** When steam is passed over hot coke, carbon monoxide and hydrogen are produced:

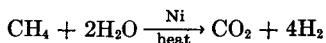


This mixture of carbon monoxide and hydrogen, called *water gas*, is of considerable value as a fuel, because both substances are combustible. If pure hydrogen is desired, the mixture is treated with steam in the presence of a catalyst to oxidize the carbon monoxide to carbon dioxide:

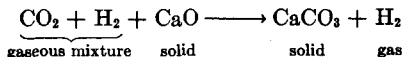


The carbon dioxide is readily removed by passing the mixture of the two gases through water under pressure. The carbon dioxide dissolves; the hydrogen does not.

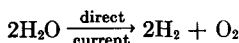
**STEAM-HYDROCARBON METHOD.** Large amounts of commercial hydrogen are made by passing mixtures of hydrocarbons and steam over a nickel catalyst at high temperatures. (Hydrocarbons are compounds that contain only carbon and hydrogen. They are the chief components of natural gas and petroleum.) The equation for the reaction involving the simplest hydrocarbon, methane, is



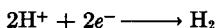
The carbon dioxide and hydrogen can be separated as described previously. Or the carbon dioxide may be removed by passing the mixture over lime (calcium oxide):



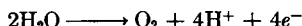
*From Water by Electrolysis.* The decomposition of water is brought about by passing a direct current through water to which a small amount of sulfuric acid has been added (Fig. 6-5). The overall decomposition reaction is as follows:



Hydrogen is evolved at the cathode:



Oxygen is evolved at the anode:



In this endothermic reaction electrical energy must be continuously supplied or the reaction will stop. The reverse process (the uniting of oxygen and hydrogen to form water) is an exothermic reaction that produces 136,640 cal of heat when 36 g of water is formed:



Conversely, when 36 g of water is decomposed by an electric current into hydrogen and oxygen, electrical energy equivalent to 136,640 cal is used. Because of the high energy requirement the preparation of oxygen and hydrogen by the electrolysis of water is too expensive for most commercial uses. However, the process is important in obtaining high-purity hydrogen and oxygen.

*Water.* Because water occurs so abundantly, our chief concern in its preparation is the purification of natural waters. If we want a

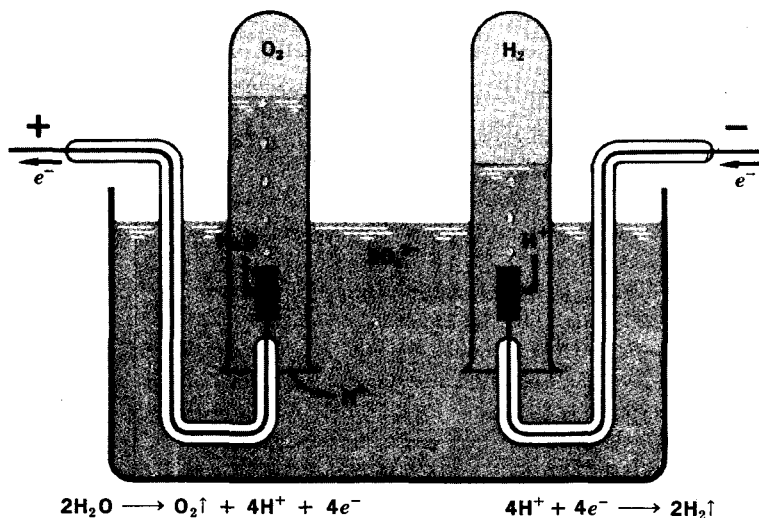


FIG. 6-5

When a direct current is passed into water containing some  $\text{H}_2\text{SO}_4$ , water molecules give up electrons at (+) electrode to release  $\text{O}_2$ . Hydrogen ions acquire electrons at the (-) electrode and form  $\text{H}_2$  molecules.

very pure type of water for laboratory work, dissolved minerals may be removed by distillation (Fig. 1-4) or by ion exchange (see page 653). Water for human consumption is generally obtained on a large scale by running river or lake water into sedimentation basins, where clay, sand, and other suspended materials are allowed to settle. The water is then filtered through sand and gravel beds to remove finely divided, suspended materials and chlorinated to kill living organisms. Adequate supply of reasonably pure water is becoming a serious problem in several areas of the United States.

## PROPERTIES OF HYDROGEN, OXYGEN, AND WATER

Many physical and chemical properties of substances can be interpreted in terms of molecular structure. Hydrogen, oxygen, and water have been studied in great detail; the latter two, especially, have unusual properties that require interpretation.

Both hydrogen and oxygen exist as stable, diatomic molecules,  $H_2$  and  $O_2$ . As described in Chap. 4, the hydrogen molecule is bonded by an electron-pair sigma bond (see Fig. 4-5). This structure is consistent with two properties of hydrogen: its zero dipole moment and its diamagnetism. On the basis of behavior in a magnetic field, substances can be classified as: *diamagnetic* if they are slightly repelled by or pushed out of the field; *paramagnetic* if they are slightly attracted by or pulled into the field; or *ferromagnetic* if they are very strongly pulled into the field.

Metals such as iron, nickel, and certain alloys are ferromagnetic. Most substances are in one of the two other classes. If they are diamagnetic, the presumption is that all electrons are paired so that the electron spins balance. Paramagnetism indicates that one or more electrons per atom, ion, or molecule are not paired. The spin attributed to each electron (see Table 3-2) gives rise to an overall paramagnetism if these spins are not paired.

Because  $H_2$  is diamagnetic, we assume its two electrons are paired; because it is nonpolar, we assume its electrons are shared equally by the two hydrogen nuclei.

The structure of the  $O_2$  molecule is not so easily pictured as the  $H_2$  molecule. Following the old rule of eight, we would simply show a double bond,  $O=O$ , consisting of two pairs of shared electrons. But this simple structure will not do, because the  $O_2$  molecule is paramagnetic and, therefore, must contain some unpaired electrons.

Several theoretical models have been suggested for  $O_2$ . One proposal is that there are three bonds, one with two electrons and two with three electrons:



Another proposal is that the  $2p^4$  electrons of each atom interact to form one sigma bond and two pi bonds (see Fig. 6-6), leaving one

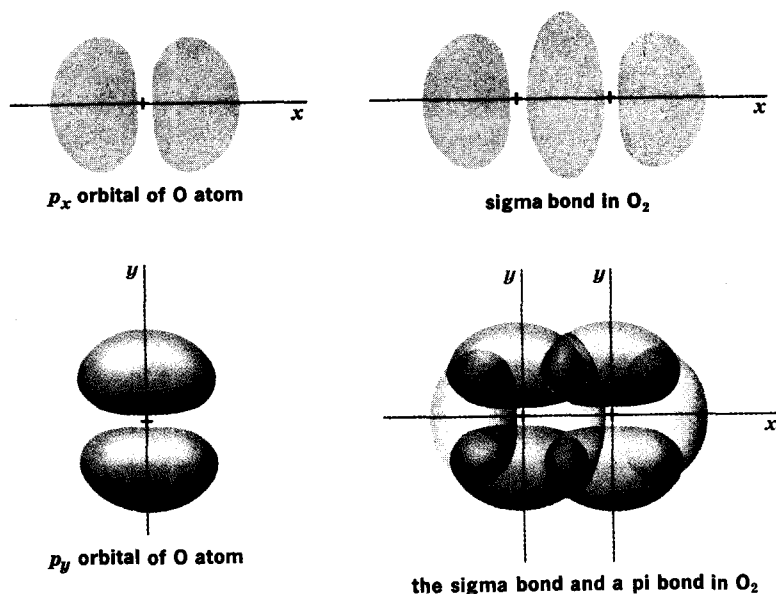


FIG. 6-6

The sigma and one of the pi bonds in an  $O_2$  molecule.

electron unpaired in a nonbonding orbital with each oxygen. Either of these proposals includes the idea that, however they are arranged, the electrons are equally held by each oxygen, because the  $O_2$  molecule is nonpolar.

Water is diamagnetic and, as pointed out in Chap. 4, has a dipole moment (see Fig. 4-11). Each hydrogen is bonded to the oxygen by a sigma bond that results from the interaction of the  $1s$  orbital of a hydrogen with one of the  $p$  orbitals of the oxygen.

The experimental value of the H—O—H bond angle of  $104^\circ$  has been accounted for in two ways. The older explanation assumes that the two unshared electrons from the  $2p^4$  electrons of oxygen (see Table 3-3) are used in bonding; the unfilled orbitals can be labeled the  $2p_y$  and  $2p_z$  orbitals, and it is recalled (see Fig. 3-11) that atomic  $p$  orbitals are at right angles. From all this, we could expect the H—O—H angle to be  $90^\circ$ . The fact that it is  $104^\circ$  is rationalized by noting that each hydrogen has a partial positive charge,  $\delta+$ , so that the hydrogens would be expected to repel one another and so widen the angle from  $90$  to  $104^\circ$ .

The more recent explanation starts by noting that a number of atoms tend to form four equivalent bonds by *hybridization* of an  $s$  with three  $p$  orbitals to give four  $sp^3$  orbitals, for example,  $CH_4$  and  $NH_4^+$ . In a perfectly symmetric molecule, these four equivalent bonds are directed toward the corners of an imaginary tetrahedron, and the bond angles are  $109^\circ28'$ . If we assume that oxygen in  $H_2O$  has hybridized  $sp^3$  orbitals, it would use two of these orbitals in

# OXYGEN, HYDROGEN, AND WATER

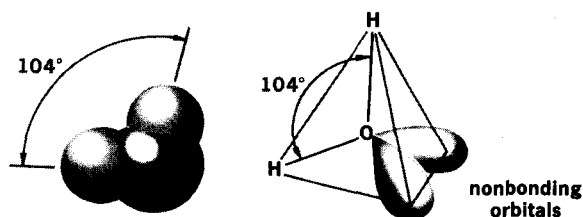


FIG. 6-7

forming bonds with the hydrogen atoms, and two other nonbonding orbitals would each consist of a pair of electrons, as shown in Fig. 6-7. The fact that the measured angle of  $104^\circ$  is less than  $109^\circ 28'$  is explained by the theory that the electrons in the nonbonding orbitals repel those in the bonding orbitals, thus pushing the O—H bonds closer together and reducing the H—O—H angle from  $109^\circ 28'$  to  $104^\circ$ .

A number of properties of hydrogen, oxygen, and water are listed in Table 6-2. The very low densities of the first two are characteristic

TABLE 6-2      *Hydrogen, oxygen, and water*

property	H <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub> O
density at 0°C	0.08987 g/liter	1.4290 g/liter	1,000 g/liter
weight of 1 mole	2 g	32 g	18 g
weight of one molecule	2 awu	32 awu	18 awu
melting point	$-259.1^\circ\text{C}$	$-218^\circ\text{C}$	$0^\circ\text{C}$
boiling point	$-252.8^\circ\text{C}$	$-183^\circ\text{C}$	$100^\circ\text{C}$
dipole moment	0	0	1.8
magnetic character	diamagnetic	paramagnetic	diamagnetic

of gaseous substances; hydrogen has the lowest density of all substances. The fact that water is a liquid at a much higher temperature than hydrogen or oxygen shows that water molecules are relatively strongly attracted to one another. The nonpolar H<sub>2</sub> molecules or O<sub>2</sub> molecules are attracted to one another only by weak van der Waals forces. The higher melting and boiling points of oxygen as compared with hydrogen are expected, because the oxygen molecule is heavier and has a more complex electronic structure that leads to greater van der Waals forces. Hydrogen has the lowest melting point of any substance except helium.

The water molecule, by contrast, is polar. Polar substances tend to have higher melting and boiling points than nonpolar ones of about the same molecular weight. Polar molecules mutually attract one another, as shown schematically in Fig. 6-8. Even compared with other polar molecules, water molecules have an unusually effective mutual attraction in that each molecule has two regions of positive and two regions of negative charge (see Figs. 4-6 and 6-7).

Because of the polar nature of water molecules, they tend to

A schematic representation of the packing of a layer of polar molecules.

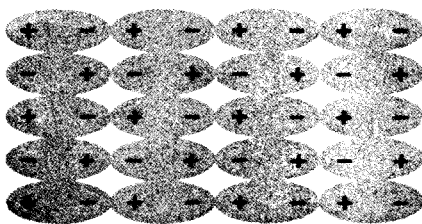


FIG. 6-8

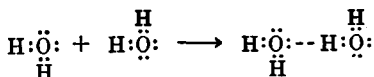
*associate* or unite with one another to form a loosely bound lattice of molecules having a pseudo-crystalline nature. Some of the experimental evidence indicating that water molecules associate is as follows:

1. The X-ray diffraction pattern of liquid water indicates that the molecules are arranged to some extent in a crystallike lattice. In most liquids, the molecules are oriented in a completely helter-skelter way.

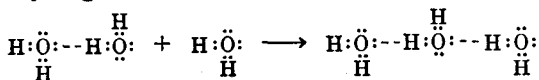
2. Molecular weight determinations of liquid water give a higher value than 18, actually from two to three times 18 at room temperature.

The degree of molecular association increases as the temperature of liquid water decreases. Therefore, we are not absolutely correct when we represent liquid water or solid water as being made up of molecules that contain two atoms of hydrogen and one of oxygen,  $H_2O$ . A more precise way is to write the formula  $(H_2O)_x$ , where  $x$  is 1, 2, 3, 4, . . . , etc. Because  $x$  is indefinite, chemists continue to write the formula as  $H_2O$ .

**The Hydrogen Bond.** The bond that is necessary to unite two simple molecules of water results from the attraction of a positive hydrogen atom of one water molecule for some of the electrons of an oxygen atom of a second water molecule. This bond, shown below by the dashed line, is referred to as the **hydrogen bond** or the **hydrogen bridge**:



Although the hydrogen bond is stronger than the van der Waals attraction between two molecules, it is not so strong as an electrovalent or a covalent bond. Because each simple water molecule contains two hydrogen atoms and two unshared pairs of electrons, this hydrogen bonding can continue until large aggregations are formed. For example,  $H_4O_2$  can react with another molecule of  $H_2O$  to form  $H_6O_3$ . The hydrogen bond is formed as follows:





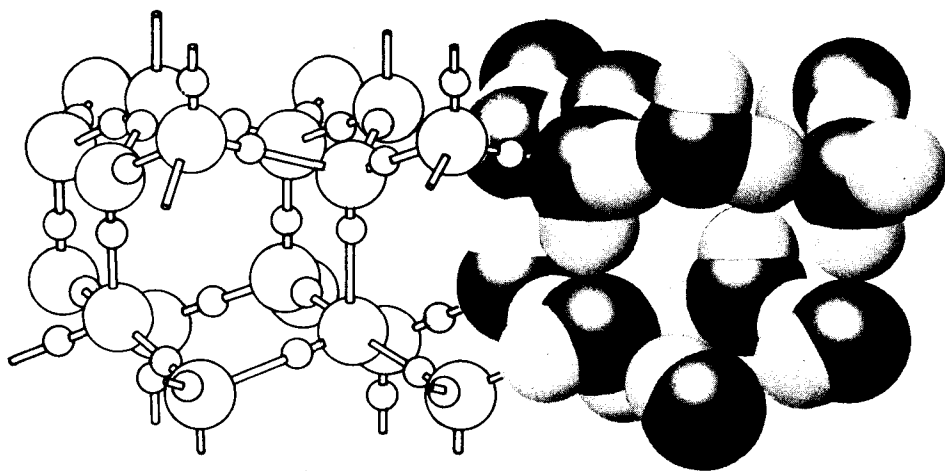


FIG. 6-9

The orderly arrangement of water molecules in ice. At the right, water molecules are shown to scale. This part of the figure merges into the portion at the left, where the hydrogen and oxygen atoms are represented by spheres, the larger ones for oxygen. The spheres are drawn to a smaller scale so that the structure may be studied more easily. Careful study of the drawing, starting with an oxygen atom in the center of the left part, reveals that each oxygen atom is connected through four hydrogen atoms to four other oxygen atoms, and that each oxygen atom has two hydrogens close to it and two farther away (connected by hydrogen bonds).

In an ice crystal, this structure extends in all directions (with the exception of the faces). As is evident from the right-hand portion of the figure, there is considerable open space in such a crystal. Hence, ice has a lower density than liquid water. The pattern in which the hydrogen bonds and the open spaces line up forms planes through the ice. A block of ice is easily cleaved along these planes with an icepick.

*Structure of Ice and Water.* From the dimensions of a water molecule it is calculated that, if these molecules were close-packed, like marbles in a box, each would occupy about 15 cubic angstroms. For a mole of water,  $6.02 \times 10^{23}$  molecules or 18 g, the calculated volume would be about 9 cc:

$$\left( \frac{15 \text{ \AA}^3}{\text{molecule}} \right) (6.02 \times 10^{23} \text{ molecules}) \left( \frac{1 \times 10^{-8} \text{ cm}}{1 \text{ \AA}} \right)^3 = 9 \text{ cc}$$

But the measured volume of a mole of water is 18 cc, or twice the calculated value. It appears, therefore, that about half of the space in water is occupied by water molecules and half is empty.

X-ray studies of ice show that each  $\text{H}_2\text{O}$  molecule has four nearest neighbors, with the overall structure featuring repeating hexagonal groupings of six molecules arranged so that large empty holes penetrate the ice crystal (see Fig. 6-9).

X-ray studies of liquid water indicate that its structure is somewhat like that of solid ice. But the fact that, on melting, the volume

occupied by the water is only about 90 per cent of the original volume of the ice indicates that the structure of the ice collapses partially and that there is less empty space in water than in ice. For a liquid to be more dense than its solid is unusual, because most substances expand on melting. This unusual behavior of  $\text{H}_2\text{O}$  is related to the structures of ice and water. Many of the hydrogen bonds are broken when ice is melted. As the ice structure collapses, the molecules become more closely packed, and the density increases. There is a further breaking up of the associated water molecules as the water is heated, and a further diminishing of the volume because of the closer packing of the molecules. The density of water is at a maximum at  $4^\circ\text{C}$ , as shown in Fig. 6-10. Above  $4^\circ\text{C}$ , the expansion due to the increased motion of the molecules becomes greater than the contraction due to the breaking up of the hydrogen bonds, and the liquid expands; that is, the molecules occupy more space. In the vapor form, the molecules have too much kinetic energy for effective bonding to occur. The molecules in water vapor actually conform to the simple formula,  $\text{H}_2\text{O}$ .

Graph showing the change in density of water with change in temperature.

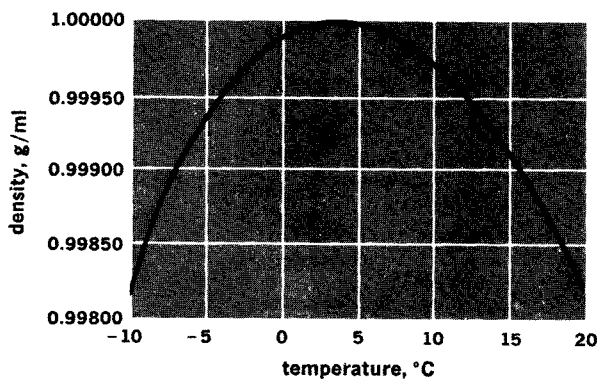
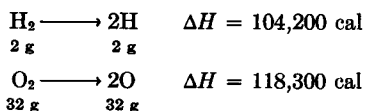


FIG. 6-10

*Chemical Properties of Hydrogen and Oxygen.* An indication of the strength of the covalent bonds in  $\text{H}_2$  and  $\text{O}_2$  molecules is given by the amount of energy that must be supplied to dissociate a mole of the molecules into atoms:



Possibly because of the strong covalent bond holding the  $\text{H}_2$  or  $\text{O}_2$  molecules together, neither hydrogen nor oxygen is very active at normal temperatures. At elevated temperatures, say from about  $300$  to  $2000^\circ\text{C}$ , oxygen readily reacts with most metals, nonmetals, and

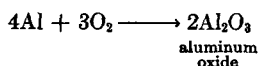
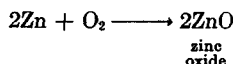
## OXYGEN, HYDROGEN, AND WATER

organic compounds. On the other hand, hydrogen, even at high temperature, does not readily combine with metals except the very active ones, such as the IA and IIA family members; but it does combine with nonmetals.

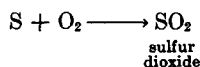
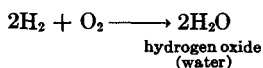
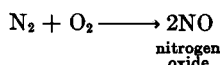
The following equations illustrate some of the characteristic reactions of these elements:

### OXYGEN

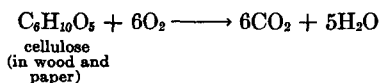
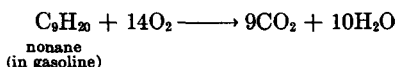
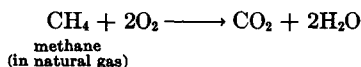
With metals:



With nonmetals:



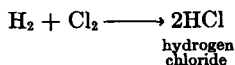
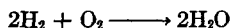
With organic compounds:

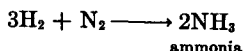
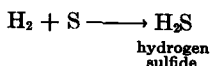


The reactions represented above are referred to as oxidation reactions. Oxidation is defined in a limited sense as a reaction in which a substance combines with oxygen. A more general definition is given on page 145. Most oxidations of the type above can proceed rapidly enough so that part of the energy is liberated as light. The reactions are then referred to as combustions.

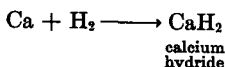
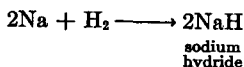
### HYDROGEN

With nonmetals:





With active metals:

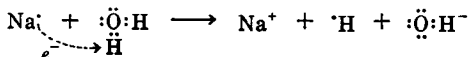


**COMMON OXIDATION STATES.** With an electronegativity of 2.1, hydrogen most often forms compounds in which it has a +1 oxidation state. Compounds are known in which hydrogen displays an oxidation state of -1, for example, metal hydrides such as NaH and  $\text{CaH}_2$ .

Oxygen, with an electronegativity of 3.5, almost always has an oxidation number of -2 in its compounds.

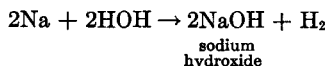
**Chemical Properties of Water.** In contrast to hydrogen and oxygen, water is quite active at room temperature and reacts readily with a great variety of substances. This statement may seem to contradict certain points made in Chap. 4. For example, water might be judged inactive, because in water molecules the outermost energy levels of hydrogen and oxygen atoms have been filled by sharing electron pairs. It must be remembered, however, that the electron pairs are unequally shared and that water molecules are highly polar. In some common reactions in which water participates, the reaction proceeds in a way so that one of the covalent bonds is broken, with the electron pair remaining with the oxygen and with the hydrogen nucleus (the proton) leaving to join some other molecule or ion.

**WITH ACTIVE METALS.** Metals in the IA family and the lower part of the IIA family have the lowest ionization energies and the lowest electronegativities of all metals. In chemical reactions, these metals have the greatest tendency to give up electrons and form positive ions. If water is the electron acceptor, an electron is acquired by one proton of the water molecule. This results in the breaking away of a neutral hydrogen atom and leaves the OH group with an electron pair corresponding to that in the covalent bond; that is, the group left is an  $\text{OH}^-$  ion:

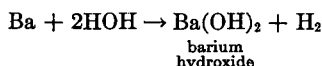


When sodium reacts with water, we observe the formation, not of atomic hydrogen, but of molecular diatomic hydrogen, so that we write

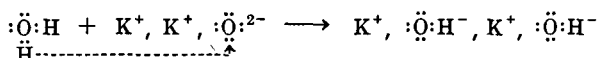
# OXYGEN, HYDROGEN, AND WATER



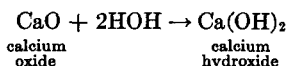
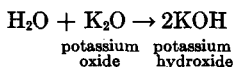
Similarly,



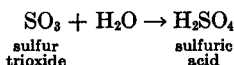
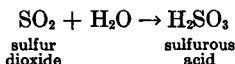
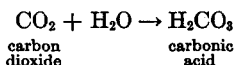
WITH OXIDES. Water often acts as an acid (a proton donor) with metallic oxides. This results in the formation of a metallic hydroxide, that is, a base. Some examples are



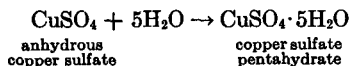
or



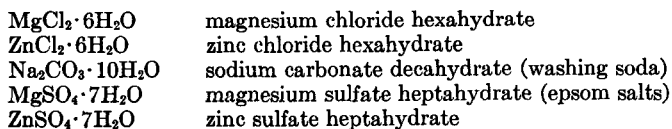
Nonmetallic oxides react with water to form acids. Examples are



FORMATION OF HYDRATES. Many salts react with water to form compounds that contain a definite number of water molecules in chemical union with the ions of the salt. For example, if copper sulfate,  $\text{CuSO}_4$ , is dissolved in water and the solution is then evaporated to the point where crystallization occurs, the crystals that separate have the composition  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The reaction is



The compound resulting from the union of the salt with water is referred to as a **hydrate**, and the pure salt is referred to as the **anhydrous compound**. Additional examples of hydrates follow:



The prefixes *hexa-*, *hepta-*, and *deca-* indicate the number of water molecules (6, 7, and 10, respectively) that are united with each apparent salt molecule. To the eye hydrates appear perfectly dry; water is present not in the liquid form, but as combined water or

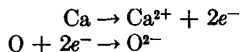
water of crystallization. For example, copper sulfate pentahydrate is dark blue and apparently perfectly dry; but when heated, it gives off water vapor and becomes the white, powdery anhydrous salt.

## OXIDATION AND REDUCTION

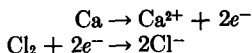
Oxidation at one time was defined as a reaction in which a substance combines with oxygen. This is an extremely common type of chemical reaction. We depend on the oxidation of the foods that we eat to supply us with energy to keep warm and do work; we oxidize common fuels to obtain the energy required for the operation of the many types of machines that have made the present era so productive of goods and foodstuffs; and we depend to some extent on oxidation reactions to rid the countryside of refuse, garbage, and sewage through the process of decay. Oxidation reactions can also be destructive, as in the burning of a building or an explosion in a coal mine.

With the advent of the modern atomic theory it has become desirable to extend the definition of oxidation to include certain reactions in which oxygen plays no part. At first glance it may appear illogical to speak of a chemical reaction as being an oxidation reaction when oxygen is not even present, but careful consideration of the following examples will show the desirability of thus extending our definition of oxidation.

First, we consider what happens to calcium atoms when they combine with atoms of oxygen. A calcium atom has two electrons in its outermost shell. During the oxidation of calcium, these electrons are transferred from the calcium to the oxygen atoms to form calcium oxide,  $\text{CaO}$ . Because of the loss of electrons, calcium atoms are changed to calcium ions:



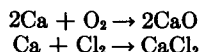
Now consider the reaction of calcium with chlorine. Here each atom of calcium loses two electrons from its outer shell as it combines with chlorine atoms to form calcium chloride. Again calcium atoms are changed to calcium ions:



The same thing happens to the calcium atom in both of these reactions: it loses two electrons, and its oxidation state increases, becoming more positive. If we refer to the first reaction as one in which calcium undergoes oxidation, we can also refer to the second in the same way. *Oxidation is defined in a broad sense as a reaction in which atoms or ions undergo an increase in oxidation state.* The agent that brings about the oxidation of calcium is oxygen in the first reaction and chlorine in the second. We refer to both chlorine and

## OXYGEN, HYDROGEN, AND WATER

oxygen as **oxidizing agents**. The overall equations for the two reactions are



The opposite process to oxidation is **reduction**. It is defined in a limited sense as a reaction in which oxygen is removed from a compound; in a broader sense it is a *process in which atoms or ions undergo a decrease in oxidation state*. Actually, both processes occur simultaneously, because an increase in oxidation state for one atom or ion is accompanied by a decrease in oxidation state for another. In the reactions above, in which calcium is oxidized by chlorine and by oxygen, these two substances are reduced; the oxidation state of the oxygen decreases from 0 to  $-2$ , and that of the chlorine from 0 to  $-1$ . Oxidation-reduction reactions are among the most common chemical reactions, and many examples are presented in later chapters.

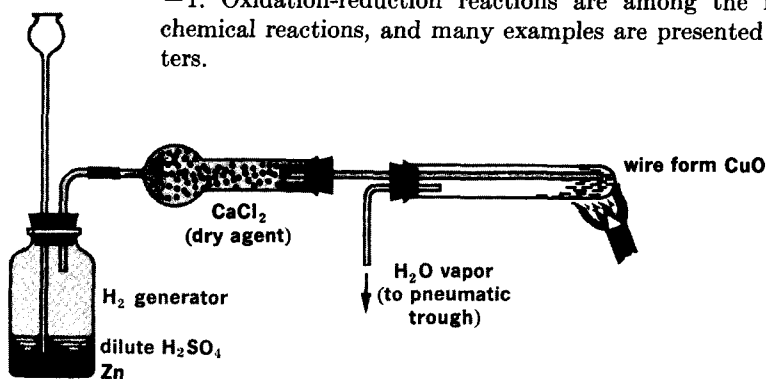


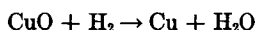
FIG. 6-11

When hydrogen is passed over hot copper oxide, copper and water are formed.

In the two reactions just taken as examples, electrons were transferred, but it is important to note that a complete transfer of electrons is not necessary in order to have changes in oxidation states. In the formation of polar covalent molecules, the pair of electrons being shared is shifted more toward one of the atoms instead of being equally shared. For example, when sulfur burns to form  $\text{SO}_2$ , atoms of sulfur and oxygen unite by sharing pairs of electrons (see Fig. 4-11). However, each electron pair is thought to be held closer to an oxygen, so that each oxygen part of the molecule is assigned an oxidation state of  $-2$ , and the sulfur part an oxidation state of  $+4$ . Sulfur is said to be oxidized, because its state changes from 0 to  $+4$ ; oxygen is reduced, its state changing from 0 to  $-2$ .

Hydrogen is an excellent reducing agent, particularly in the reduction of metallic oxides. This may be demonstrated by passing hydrogen over hot copper oxide (Fig. 6-11). The black copper oxide

rapidly disappears and is replaced by a solid that is the color of metallic copper; water meanwhile appears in the cooler part of the test tube. The following equation describes the reaction:



The copper ion is reduced (its oxidation state decreases from +2 to 0); the hydrogen is the reducing agent (its oxidation state increases from 0 to +1).

## ACTIVITY SERIES OF METALS

When the common metals are arranged in the order of decreasing tendency to lose electrons, that is, to be oxidized by other ions in solution, we have what is called the **activity series** (or electrochemical series) of the metals, shown in Table 6-3. In the table the most active metal heads the list, and the least active one comes last. Hydrogen is included, because the reactions involving metals and acids are common and important.

*Activity series of metals*

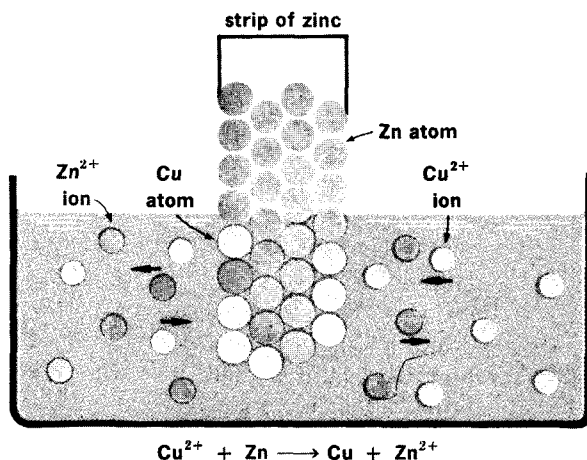
TABLE 6-3

Rb	} violent reaction with $\text{H}_2\text{O}$			
K				
Ca	} slow reaction with $\text{H}_2\text{O}$			
Mg	} react with steam			
Al				
Mn				
Zn				
Cr				
		displace $\text{H}_2$ from acids	combine directly with oxygen	oxides easily reduced by $\text{H}_2$ at elevated temperatures to free metals and $\text{H}_2\text{O}$
Fe				
Ni				
Sn				
Pb				
H				
Cu				
Bi				
Sb				
Hg	} oxides decompose when heated			
Ag				
Pt				
Au				

We generally think of metals reacting with nonmetals, but a metal also reacts with the positive ion of a second metal, provided the second metal is below the first one in the activity series (see Fig.



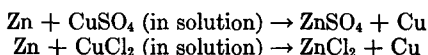
# OXYGEN, HYDROGEN, AND WATER



When a strip of zinc is placed in a solution of copper sulfate, copper ions gain electrons from zinc atoms.

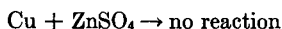
FIG. 6-12

6-12). This type of reaction is referred to as a *displacement* reaction. For example, zinc is placed above copper in the activity series, because metallic zinc displaces copper from copper compounds. Such reactions show that zinc has a greater tendency to lose electrons than does copper:

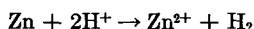
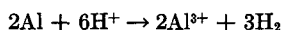


In these reactions, elemental zinc is oxidized to zinc ions, and the copper ions are reduced to elemental copper.

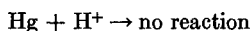
The reverse reaction does not occur to an appreciable extent:



In the preparation of hydrogen by the action of a metal with an acid, any metal above hydrogen in the activity series is capable of reacting with hydrogen ions:



Metals below hydrogen are not attacked by the hydrogen ions of acids:



This type of oxidation-reduction reaction has many useful applications, as in obtaining metals from their compounds and in producing current with storage and flashlight batteries.

## ISOTOPES

Three isotopes each of oxygen and hydrogen have been identified among the naturally occurring elements or their compounds. These are  $^{16}\text{O}$ ,  $^{17}\text{O}$ ,  $^{18}\text{O}$ ,  $^1\text{H}$ ,  $^2\text{H}$ , and  $^3\text{H}$ . About 99.8 per cent of all the oxygen atoms existing in nature are of the  $^{16}\text{O}$  variety, and about 99.98 per cent of all natural hydrogen atoms are  $^1\text{H}$ . This means that in a sample of water the vast majority of molecules are of the  $^1\text{H}^1\text{H}^{16}\text{O}$  type. However, also present are relatively small numbers of molecules, such as  $^2\text{H}^1\text{H}^{16}\text{O}$ ,  $^2\text{H}^2\text{H}^{16}\text{O}$ ,  $^2\text{H}^2\text{H}^{17}\text{O}$ ,  $^1\text{H}^1\text{H}^{17}\text{O}$ .

Because of their great relative differences (for example,  $^2\text{H}$  is twice as heavy as  $^1\text{H}$ ), the isotopes of hydrogen have less resemblance to one another than do isotopes of other elements. Hydrogen isotopes are even identified by special names, whereas mass numbers suffice for all other isotopes. Table 6-4 gives the special names, special symbols, and a comparison of some of the properties of the hydrogen isotopes. Deuterium is also called **heavy hydrogen**.

*Isotopes of hydrogen*

TABLE 6-4

name and symbol	$^1\text{H}$ or H protium	$^2\text{H}$ or D deuterium	$^3\text{H}$ or T tritium
atomic mass, awu	1.0078	2.0142	3.0160
freezing point, $^{\circ}\text{C}$	-259.1	-254.4	
boiling point, $^{\circ}\text{C}$	-252.7	-249.6	
stability of nucleus	stable	stable	unstable; half of any sample decays to $^3\text{He}$ in 12.5 years

## HEAVY HYDROGEN AND HEAVY WATER

Deuterium and deuterium oxide (heavy water)<sup>1</sup> are now produced in the United States at the rate of several tons a month. Presumably, part of this output is for use in hydrogen bombs. Some of it is for peacetime operations involving the use of heavy water as a moderator in uranium reactors (Chap. 15) and the use of heavy hydrogen in tracer research and in experimental thermonuclear reactors (Chap. 15).

The separation of two isotopes is usually difficult. It is relatively easy in the case of hydrogen, because there is a greater difference in properties between the isotopes of hydrogen than between the isotopes of any other element. Even so, the separation is tedious and expensive, because the ratio by atoms of deuterium to protium in natural hydrogen compounds is only about 1:7,000. Separation is

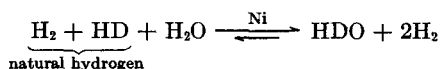
<sup>1</sup> The term "heavy" water refers specifically to water molecules in which the hydrogen has a mass number of 2. Conceivably, heavy water molecules could be  $^2\text{H}_2^{16}\text{O}$ ,  $^2\text{H}_2^{17}\text{O}$ , and  $^2\text{H}_2^{18}\text{O}$ . Actually, because the oxygen isotope of mass number 16 is extremely abundant, heavy water is composed principally of  $^2\text{H}_2^{16}\text{O}$  molecules.

usually accomplished by combining two or more of the following methods:

1.  $D_2O$  and  $HDO$  have slightly higher boiling points than  $H_2O$ . Repeated fractional distillations of water therefore achieve some separation of  $D_2O$ ,  $HDO$ , and  $H_2O$ .

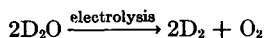
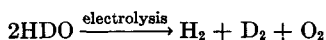
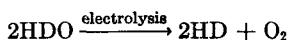
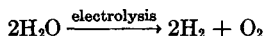
2. The boiling points of the elemental isotopes differ by a wider margin than do the boiling points of compounds of the isotopes. Repeated distillations of liquid hydrogen bring about a separation of the isotopes. However, the practical difficulties of distilling a liquid that boils at  $-253^\circ C$  are great.

3. When  $H_2$ ,  $HD$ , and water are passed over a nickel catalyst, the following exchange tends to take place:

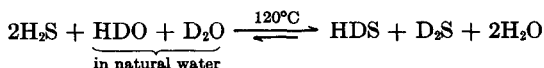


This results in a considerable increase in the deuterium content of water.

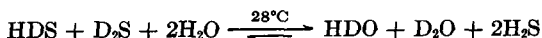
4. During the electrolysis of water,  $H_2O$  molecules are electrolyzed more rapidly than  $D_2O$  or  $HDO$  molecules. Heavy water,  $D_2O$ , tends to remain behind in the cell, whereas  $H_2O$  molecules are decomposed into  $H_2$  and  $O_2$ . The following equations show the reactions that may occur. The reactions are arranged in decreasing order of their tendency to take place.



5. When hydrogen sulfide,  $H_2S$ , gas is passed through water under pressure at about  $120^\circ C$ , the protium of hydrogen sulfide tends to exchange with deuterium of water:



On cooling the enriched hydrogen sulfide and bubbling the gas through water at  $28^\circ C$ , the reverse exchange tends to take place:

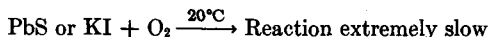
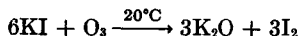
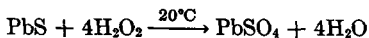


Bubbling enriched hydrogen sulfide through a relatively small quantity of cool water greatly increases the percentage of  $D_2O$  and  $HDO$  in the small amount of water.

In a large plant located on the Savannah River in South Carolina and owned by the Atomic Energy Commission, three of these processes are combined to produce hydrogen, either in the form of the element or as heavy water that is 98.5 per cent deuterium oxide.

## OZONE AND HYDROGEN PEROXIDE

Ozone and hydrogen peroxide,  $O_3$  and  $H_2O_2$ , respectively, have one important property in common. Both are composed of unstable molecules that can participate in oxidation reactions at temperatures at which ordinary oxygen is inactive. For example:



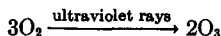
The oxidation of mercury and silver further illustrate this point. At normal temperatures, these two metals are oxidized by ordinary oxygen at an imperceptible rate, if at all. When placed in ozone, they rapidly become coated with an oxide film (become tarnished) because of the oxidizing action of ozone. Both ozone and hydrogen peroxide tend to decompose on standing, as follows:



Ozone is a pale blue gas with a characteristic odor, and hydrogen peroxide is a colorless liquid. Both are hazardous chemicals. Hydrogen peroxide in a concentrated form tends to explode violently when not handled properly. The common household variety is a 3 per cent  $H_2O_2$  solution in water and is not dangerous at this dilution.

Elements that exist in more than one form are said to be **allotropic** (Gr. *allos tropos*, other way), and the forms are referred to as **allotropes**. Ordinary oxygen and ozone are allotropes of the element oxygen.

Most of the elemental oxygen in the outer reaches of the atmosphere is believed to be in the form of ozone, owing to the action of ultraviolet rays from the sun on ordinary oxygen:



This action by oxygen molecules prevents most of the ultraviolet rays from reaching the earth's surface, thus giving man a protective screen from this type of harmful radiation. Of course, traces of ozone are formed at lower elevations also. The reaction is believed to proceed as follows: oxygen molecules absorb the radiant energy and dissociate into oxygen atoms, which then combine with other  $O_2$  molecules to form  $O_3$  molecules.

Oxygen in the vicinity of electrical motors and other electrical apparatus may also be converted into ozone. However, the amount produced in this way is not great.

Continued breathing of air with as little as 0.1 part of ozone per 1 million parts of air produces headaches and other symptoms. Ozone in the air in some large cities is now considered a health hazard. It

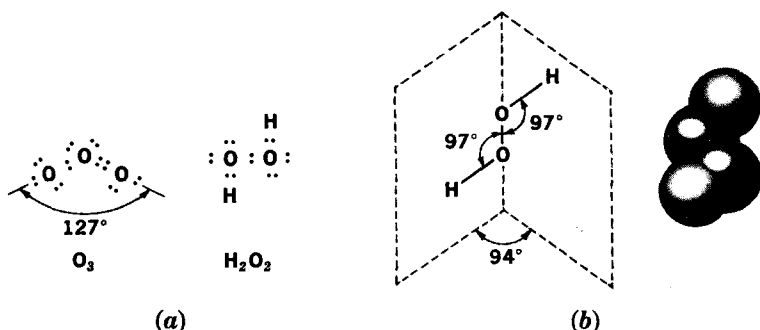


FIG. 6-13

(a)

(b)

The structures of  $O_3$  and  $H_2O_2$  molecules.

apparently is produced by the action of sunlight on polluted air.

The structures of ozone and hydrogen peroxide molecules are shown in Fig. 6-13.

**Bleaching.** Many natural materials are slightly colored because of the presence of small amounts of complex organic compounds. For example, flour, cellulose materials, and vegetable oils are usually slightly colored when first obtained from their plant sources. To obtain a colorless product, the colored compounds are oxidized to colorless compounds. The process is referred to as **bleaching**, and the oxidizing agent employed is called a **bleaching agent**. Ordinary oxygen is not a suitable bleaching agent, because a rather high temperature is required to start the oxidation. Furthermore, once started, both the pigment and the product oxidize, and combustion may even occur. On the other hand, ozone and hydrogen peroxide react with many pigments at room temperature and convert them into colorless substances. The less active starch, cellulose, fat, and protein molecules are not affected. Impurities that give rise to objectionable odors and tastes are also removed from certain foods by mild oxidation in which ozone is the oxidizing agent. Chlorine, another effective bleaching agent, is discussed in Chap. 21.

**Preparation. OZONE.** Ozone is commonly prepared by allowing a silent electric discharge to pass through oxygen. A simple *ozonizing* apparatus is shown in Fig. 6-14. It consists of two glass tubes, one enclosing the other. Aluminum foil is wrapped around each tube and connected through two wires to a source of high-voltage current. When the current is on, the two pieces of foil becomes highly charged, so that there is a "silent" electrical discharge from one to the other. Some of the oxygen passing between the two pieces of metal during the discharge is converted to ozone. This discharge, observable in a dark room as a blue glow extending from one foil to the other, gives a better yield of ozone than does a spark discharge, which produces

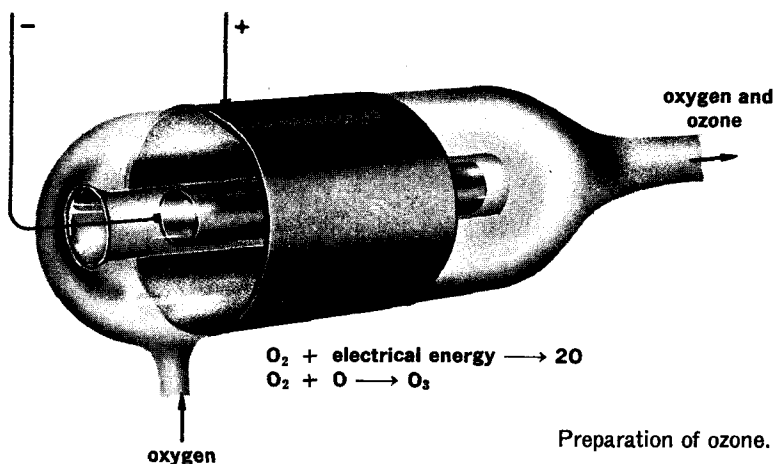
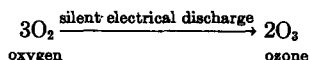
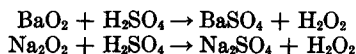


FIG. 6-14

a high temperature in the vicinity of the spark (or arc). When pure dry oxygen at 20°C is passed through the apparatus, about 19 per cent is converted into ozone; at the temperature of liquid air about 90 per cent is converted. The equation for the reaction is



**HYDROGEN PEROXIDE.** Dilute water solutions of hydrogen peroxide can be obtained by treating barium peroxide or sodium peroxide with dilute acids:

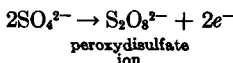


Hydrogen peroxide is now made in commercial quantities by a process that begins with the electrolysis of concentrated sulfuric acid at low temperature. The reactions are:

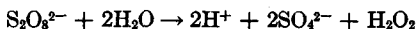
At the cathode:



At the anode:



The process is completed by adding water to the mixture and warming. Water reacts with the peroxydisulfate ion to form an aqueous solution of sulfuric acid and hydrogen peroxide:



We may look on the entire process as an indirect method of oxidizing water,  $\text{H}_2\text{O}$ , to hydrogen peroxide,  $\text{H}_2\text{O}_2$ .

The dilute solutions may be concentrated by distillation, an operation that must be carried out with extreme care, because impurities

catalyze the violent decomposition of hydrogen peroxide. Common commercial concentrations are 27.5, 35, 50, and 90 per cent solutions. Hydrogen peroxide of approximately 100 per cent concentration is also manufactured.

### **COMMERCIAL IMPORTANCE OF HYDROGEN AND OXYGEN**

We continually improve our standard of living by studying the properties of matter and then applying what we have learned to increase the efficiency of the implements that we build and the processes that we use.

Consider hydrogen. With the discovery of this element late in the eighteenth century and the development of efficient methods in the nineteenth and twentieth centuries of preparing it on a large scale from water, coal, and petroleum, a new and valuable substance was made available for man's use. Some of the developments that have resulted from the work on hydrogen are:

1. An era of air travel in the early part of the twentieth century by means of hydrogen-filled balloons and zeppelins.
2. The synthesis of many compounds, including ammonia and wood alcohol. The synthesis of ammonia from nitrogen and hydrogen makes possible the large-scale production of nitrogen-containing fertilizers and has resulted in a tremendous increase in the productivity of soils.
3. The reaction of hydrogen with certain organic compounds (hydrogenation, see Chap. 26) gives hydrogenated fats for foods and for cooking, superior gasolines and lubricating oils, and many other useful products.
4. The combustion of hydrogen,  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{heat}$ , is employed in torches to produce high temperatures for working metals and for the propulsion of rockets.

Consider oxygen. With the discovery that oxygen is the oxidizing agent for the combustion of all common fuels and for the oxidations that go on in the cells of organisms, it became possible to work out ways of using this substance more effectively. Because air is a dilute source of oxygen (21 per cent) the first step was to get oxygen in a more concentrated form by separating it from air (commercial oxygen now ranges from about 95 to 99.5 per cent oxygen). Combustion reactions proceed more rapidly in the concentrated oxygen than in dilute oxygen (air), so that higher temperatures can be reached; and the heat loss is reduced because nitrogen (78 per cent of air) is not present to carry away heat energy. Further, it is more efficient to transport pure oxygen than dilute oxygen, a fact important to aviators and divers. These developments have resulted in the use of commercial oxygen in:

1. Blast furnaces and open-hearth furnaces for the production of

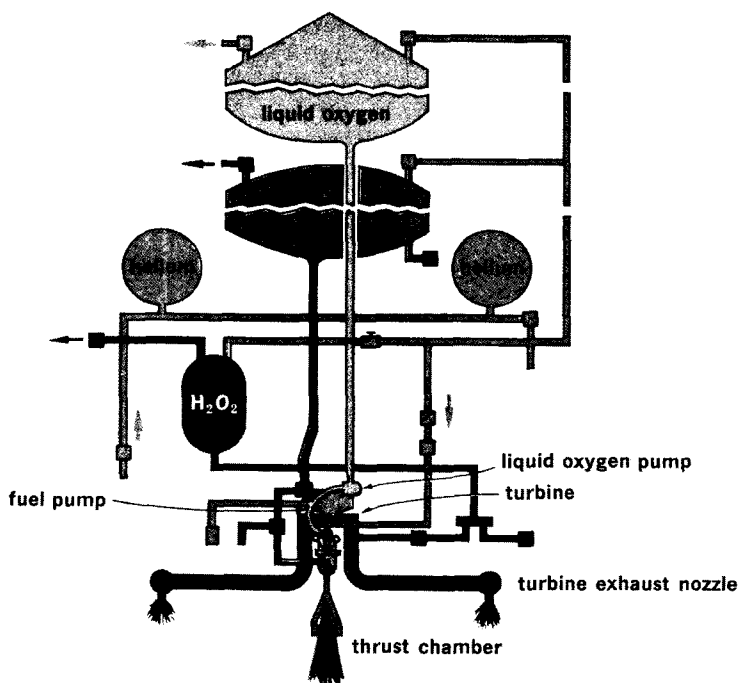


FIG. 6-15

The first stage of the Vanguard rocket. A turbine-operated unit pumps the propellant (liquid oxygen and kerosene in this case) to the injector in the thrust chamber. The gas to drive the turbine is generated by the catalytic decomposition of hydrogen peroxide. To help maintain a constant flow of fuel and oxidizer, helium gas is maintained at constant pressure over each. Various valves for filling the tanks and for controlling flow are indicated schematically. (Courtesy of The Martin Company.)

iron and steel. The steel industry is by far the biggest user of commercial oxygen.

2. The propulsion of rockets (Fig. 6-15).
3. Oxyacetylene and oxyhydrogen torches.
4. Respiration devices in hospitals, airplanes, mines, underwater vessels, etc.

## OXYGEN-CARBON DIOXIDE CYCLE IN NATURE

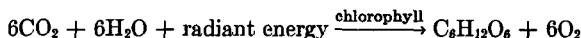
In respiration in man and other animals, the inhaled air is brought into contact with blood in the lungs. There the dark red hemoglobin of the venous blood reacts with a certain amount of the oxygen to form oxyhemoglobin, the bright red component of arterial blood. This oxyhemoglobin is transported through the arteries to the cells, where the oxygen is used in the oxidation of food to carbon dioxide, water, and other products. The carbon dioxide is picked up



by the blood, largely as the bicarbonate ion, and along with hemoglobin is transported through the veins to the lungs. The carbon dioxide is liberated in the lungs and exhaled, and the cycle starts anew. The oxidation reactions in the cells liberate the energy that keeps us warm and enables us to do work.

The energy to operate an automobile or a steam locomotive or to heat homes with stoves or furnaces is derived in the same general way from the oxidation of gasoline, coal, and other fuels. In such activities man is constantly removing oxygen from the air and converting it mainly to carbon dioxide and water. But we do not have to worry about the supply of oxygen becoming exhausted, because growing plants take up carbon dioxide and water, convert them into sugars, starch, and cellulose, and return oxygen to the air. This cycle in nature keeps the amount of elementary oxygen relatively constant.

The first balanced equation<sup>1</sup> below represents the formation of sugar in plants by photosynthesis; the second, the oxidation of sugar in the cells of a human being:



It is interesting to note that human beings cannot live long if the oxygen in the air is reduced to about one-half of its normal amount, nor do common fuels burn satisfactorily at this low concentration of oxygen.

*The Storing of Energy.* The first equation above shows the utilization of energy from the sun to regroup the atoms in carbon dioxide and water into molecules of higher energy, molecules of sugar and oxygen. This kind of energy is often spoken of as the **chemical energy** of a substance.

When molecules with high chemical energy change to molecules with lower chemical energy, heat, light, mechanical, or electrical energy is given off. The second equation shows that  $\text{C}_6\text{H}_{12}\text{O}_6$  and  $6\text{O}_2$  must have more chemical energy than  $6\text{CO}_2$  and  $6\text{H}_2\text{O}$ . During the chemical reaction some of the chemical energy of the sugar and oxygen is converted to heat energy.

The photosynthesis reaction in plants is an endothermic process, the energy coming from the sun. The energy we obtain by burning any fuel, for example, coal, wood, or food, comes indirectly from the sun.

<sup>1</sup> These are overall equations that do not represent all the complex reactions necessary to convert the reactants into the products. In woody plants a large proportion of the end product is cellulose,  $(\text{C}_6\text{H}_{10}\text{O}_5)_x$ .

### Terms

Phlogiston, calyx, laboratory and commercial preparations, pyrolysis, catalyst, diamagnetic, paramagnetic, ferromagnetic, paired spins, hydrogen bond, ice structure, oxidation, reduction, oxidation state, hydrate, anhydrous, water of crystallization, oxidizing agent, reducing agent, activity series of metals, displacement reaction, allotropic, allotropes, bleaching agent, oxygen-carbon dioxide cycle.

### Exercises

1. One gram of filter paper is burned in apparatus so that the products of the combustion can be collected and weighed. Are their weights 1 g, less than 1 g, or more than 1 g? Why?
2. Describe, with the aid of a diagram, how you might experimentally carry out the combustion of 1 g of filter paper, collect the products of the combustion, and determine their weights.
3. Refer to Exercise 1. Can your predicted weight of the products be accounted for in terms of the phlogiston theory? How? In terms of Lavoisier's theory of combustion? How?
4. Priestley observed that a candle burned more brilliantly, and that a mouse lived longer, in a volume of his "dephlogisticated" air than in an equal volume of air. How did he account for these differences? How would you account for them?
5. Why did Lavoisier choose the names hydrogen and oxygen for these elements?
6. State briefly why the commercial preparation of oxygen is not a very suitable laboratory method, and why the method we commonly use in the laboratory is not suitable for industry.
7. A solid mixture of sodium chlorate and iron(III) oxide weighing 2.00 g is heated at about 350°C for a period of time. After cooling, the mixture is found to weigh 1.50 g. Account for the loss in weight.
8. Complete and balance the following equations:  
$$\text{Mg} + \text{HBr} \rightarrow$$
$$\text{Sr} + \text{H}_2\text{O} \rightarrow$$
$$\text{K} + \text{CH}_3\text{OH (methyl alcohol)} \rightarrow$$
$$\text{Fe} + \text{H}^+ \rightarrow$$
$$\text{Zn} + \text{H}_3\text{O}^+ \rightarrow$$
$$\text{Ba}(\text{ClO}_3)_2 \xrightarrow{\text{heat}}$$
$$\text{KNO}_3 \xrightarrow{\text{heat}}$$
9. Suggest a reason why it is more economical to obtain large amounts of oxygen from air than from water.

**OXYGEN, HYDROGEN,  
AND WATER**

10. Could you prepare some hydrogen by using chemicals and apparatus that you could find in your home? Show, with a diagram, how you would use the apparatus; write the equation for the reaction.
11. Hydrogen is diamagnetic, and oxygen is paramagnetic. What does this mean in terms of the behavior of hydrogen and oxygen molecules in magnetic fields; in terms of the structures of hydrogen and oxygen molecules?
12. Based on orbital theory, we might conclude that the bond angle in water is  $90^\circ$ . Why? Experimentally, we find the angle to be  $104^\circ$ . How is orbital theory used to account for this angle?
13. Water molecules tend to become oriented or turned in a definite way in an electrical field, and hydrogen and oxygen molecules do not. Why?
14. Most substances contract on changing from the liquid to the solid state. Water expands. Account for this unusual behavior of water.
15. What is meant by hybridization of bonding orbitals? Give examples.
16. A given volume of water has a maximum weight at  $4^\circ\text{C}$ . Account for this in terms of the structure and behavior of water molecules.
17. Write an equation for the combustion in air of each of the following: magnesium, ethane ( $\text{C}_2\text{H}_6$ ), sugar ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ), phosphorus, hydrogen. Are all these reactions appropriately referred to as oxidation reactions? Why?
18. Under certain conditions, we might refer to the reaction of iron with oxygen as both oxidation and combustion; under other conditions, as only oxidation. Explain.
19. What is the oxidation state of each element in the following:  $\text{K}_2\text{O}_2$ ,  $\text{LiH}$ ,  $\text{CaO}$ ,  $\text{O}_2$ ,  $\text{HCl}$ ?
20. A certain compound was crystallized from a water solution and then allowed to dry between layers of filter paper. A sample of the dry compound weighing 2.00 g was heated below its melting point for 30 min. During this period the crystals crumbled to a powder but did not melt. After cooling, the sample was found to weigh 1.50 g. On standing in an open container for several hours, the sample was again weighed. The weight was 1.90 g. Give a possible explanation of these results.
21. Give an example of a molecule in which two atoms are joined by a sigma bond resulting from the overlap of s orbitals.
22. Summarize the evidence that indicates that water molecules are polar.
23. Compare the number of moles of  $\text{H}_2\text{O}$  in 1 ml of solid water at  $0^\circ\text{C}$  and in 1 ml of liquid water at  $0^\circ\text{C}$ ; in 1 g of solid water at  $0^\circ\text{C}$  and in 1 g of liquid water at  $0^\circ\text{C}$ ; in 1 ml of liquid water at  $0^\circ\text{C}$  and in 1 ml of liquid water at  $3^\circ\text{C}$ .
24. Which is preferable to say, "Water contains hydrogen and oxygen," or "Water is made of hydrogen and oxygen"? Justify your choice.
25. What is the weight of a mole of hydrogen atoms; of hydrogen molecules?

26. How much energy must be supplied to bring about the dissociation of 1.0 g of hydrogen molecules into hydrogen atoms; of 1.0 g of oxygen molecules into oxygen atoms?
27. How many moles of water will be formed when 1 mole of hydrogen molecules combines with oxygen? What will this quantity of water weigh?
28. Write balanced equations for the following chemical reactions; in each case, indicate what needs to be done, if anything, beyond bringing the reactants together, for the reaction to occur:
  - a. strontium and water  $\rightarrow$
  - b. sodium oxide and water  $\rightarrow$
  - c. calcium and water  $\rightarrow$
  - d. nitrogen pentoxide ( $\text{N}_2\text{O}_5$ ) and water  $\rightarrow$
  - e.  $\text{MgCl}_2$  (anhydrous) and water  $\rightarrow$
29. On the basis of the activity series, predict whether a reaction will occur in the following cases, writing equations for those which will:
  - a. Zinc in a water solution of mercury(II) chloride
  - b. A piece of silver in aqueous potassium nitrate
  - c. Gold in dilute hydrochloric acid
30. When magnesium metal is placed in dilute  $\text{HCl}$ , the magnesium reacts rapidly with the acid. Write an equation showing only the atoms and ions that are involved in the reaction. What underwent oxidation; reduction; acted as the oxidizing agent; acted as the reducing agent?
31. Which mixture would be more difficult to separate into its component parts, a mixture of  $^{35}\text{Cl}_2$  and  $^{37}\text{Cl}_2$  or a mixture of  $^{127}\text{Te}$  and  $^{127}\text{I}_2$ ? Why?
32. Of what importance is deuterium?
33. Discuss, from the point of view of orbital theory, the bonds in a hydrogen peroxide molecule.
34. Equal weights of carbon are completely burned in pure oxygen and in pure ozone:
  - a. Is the weight of carbon dioxide formed the same in each case? Explain.
  - b. Does the weight of oxygen used in the combustion equal that of the ozone used? Explain.
  - c. Is the amount of heat given off the same for each combustion? Explain.
35. Why is ozone a more satisfactory bleaching agent than oxygen?
36. Discuss the different methods of preparing hydrogen peroxide.
37. Contrast the chemical properties of the two oxides of hydrogen.
38. If we permanently lost all our manufacturing facilities for the production of elemental hydrogen, here and abroad, how might the way of life of your generation be affected; of the next generation?
39. Photosynthesis of carbohydrates in plants depends on radiant energy from the sun. What happens to this energy?
40. The density of ice at  $0^\circ\text{C}$  is 0.917 g/ml. Which has the larger volume, 1 lb of ice at  $0^\circ\text{C}$  or 1 lb of water at  $0^\circ\text{C}$ ? By what per cent?

**OXYGEN, HYDROGEN,  
AND WATER**

41. What is the weight in grams and in pounds of 1 liter of water at room temperature? How many moles of water are present? What limits the number of significant figures that you use in these calculations?

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## STATES OF MATTER;

## KINETIC THEORY



*States of matter.* The matter of the universe exists in three *states*: solid, liquid, and gaseous. These three states are so readily recognized that our only need here is to organize the facts that we already know.

A gas has no shape of its own; rather it takes the shape of its container. It has no fixed volume, but is compressed or expanded as its container changes in size. The volume of the container is the volume of the gas.

A liquid has no specific shape; it takes the shape of its container as it seeks its own level under the influence of gravity. But it does have a specific volume. Although it is not absolutely incompressible, it is compressed a negligible amount even by moderately high pressures.

A solid has a fixed shape and a fixed volume. Like a liquid, it is not compressed appreciably by moderately high pressures.

### GASEOUS STATE

Each elemental substance may exist as a gas, liquid, or solid, depending on the temperature. Many compounds, however, can exist only in the solid state, or at the most, the solid and liquid states, because they are unstable at elevated temperatures. Ordinary sugar, for example, decomposes instead of melting when heated; potassium chlorate melts to a clear liquid that decomposes rather than vaporizing when heated further. Water is a familiar example of a compound that can exist in all three states.

When substances such as oxygen, iron, water, and carbon dioxide are in the gaseous state, they possess certain properties that are not significant when these same substances are in the liquid or solid state.

**Compressibility.** All gases are easily compressed. Most of us have had experience in pumping air into bicycle or automobile tires. Air is a mixture of gases that behaves physically in the same manner as pure oxygen, or pure nitrogen, or any other gaseous substance. We can put into a tire a volume of air that is initially two or three times the volume of the tire. If the tire is punctured, the air, over and above the amount equal to the volume of the tire, will rush out. Such behavior, too, is characteristic of all gases. This, the opposite of compressibility, is called expansibility.

**Effect of Temperature.** Unless they are confined in rigid closed containers, all gases expand when heated and contract when cooled. Such action can be checked visibly if the gas is in a vessel whose volume can be varied, for example, a rubber balloon or a cylinder that is closed with a movable piston.

If a gas is trapped in a leak-proof container of constant volume, like a steel tank, the pressure exerted by the gas rises if its temperature goes up, and falls if its temperature goes down.

**Diffusion.** A drop of perfume slowly evaporates, and the fragrant gas announces the presence of the wearer. One gas can *diffuse* through another quite easily—in this case, perfume through air.

**Liquefaction.** If a gas is cooled to a sufficiently low temperature, it changes from a gas to a liquid. The liquid has a volume much smaller than that of the gas, usually about 1/1,000 the volume of the gas under normal conditions of temperature and pressure.

**Gaseous State: Facts and Theories.** From the characteristics of gases scientists have built up a reasonable theoretical picture of the fundamental structure of a gas. Below are listed some of the experimental facts, and opposite each is stated a part of the theory that it supports:

fact	theory
No particles are visible in gases, but a gas has weight. Furthermore, a given weight of gas uniformly fills any size of container. It leaks (diffuses) from the container through pores that are invisible under a microscope.	Gases are made up of particles too small to be seen with the most powerful microscope. These particles, called molecules, are in rapid random motion, so that they move into all parts of a containing vessel, no matter how large. Their motion and small size permit them to pass through tiny pores.
When the pressure on it is released, a gas expands.	The molecules move in random directions and have very little attraction for one another.
The volume of a certain quantity of gas can be greatly decreased by compressing the gas.	The molecules of the gas are forced closer together by an increase in pressure.

fact

theory

If a gas is compressed sufficiently, and perhaps cooled at the same time, it liquefies.

For a given weight of substance, the volume it occupies as a gas is much greater than that which it occupies as a liquid.

In a closed container a gas exerts uniform pressure on every part of the wall of the container.

In a closed container a gas exerts a certain pressure. As long as the volume remains the same and no heat is gained or lost, the pressure remains the same indefinitely.

In a closed container of definite volume, a gas exerts a certain pressure so long as the temperature is not changed. If the gas is heated, the pressure rises. If the gas is cooled, the pressure falls.

A moving body such as a golf ball or a hammer has an amount of kinetic energy that depends on two quantities: the mass of the body and its speed or velocity. Expressed as an equation:  $KE = \frac{1}{2}mv^2$ .

Experiments show that dense gases diffuse more slowly than less dense gases at the same temperature.

The molecules of a gas do have some attraction for one another. The attractive force is enough to hold the particles together as a liquid under the proper conditions.

The molecules of a gas are widely separated at ordinary temperatures and pressures.

The moving molecules hit the walls of the container at random. The pressure of the gas is the sum of the pressures exerted by the billions upon billions of moving molecules.

The collisions of the molecules result in no loss of energy. If energy were lost, the temperature and pressure would fall. The collisions are thought to be perfectly elastic; that is, there is no net change in kinetic energy.

As the temperature rises, the molecules move more rapidly and hit the wall harder and more often at higher temperatures. The present theory holds that the kinetic energy of the molecules is directly proportional to the absolute temperature (see page 164).

The fact that the expression  $KE = \frac{1}{2}mv^2$  holds for all known moving bodies is good reason for believing that it also holds for the moving molecules of gases.

At a given temperature, heavy molecules move more slowly than lighter ones; their average kinetic energies are equal.

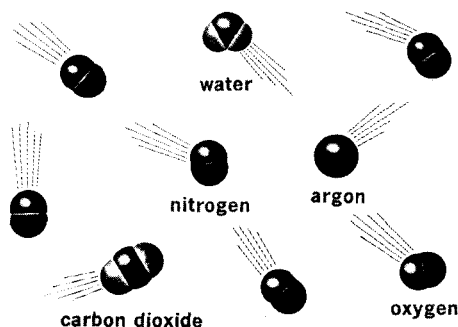
The points above constitute the moving-particle theory of gases, or, to use the language of the scientist, the kinetic-molecular theory of gases. The theory may be summarized as follows:

1. Gases are composed of molecules that are widely separated from one another in otherwise empty space.
2. The molecules move about at high speeds, traveling in straight paths but in random directions.
3. The molecules collide with one another, but the collisions are perfectly elastic (result in no loss of energy).
4. The average velocity of the molecules increases as the temper-



ature increases and decreases as the temperature decreases. Individual molecules in a sample of a pure gas are not all moving at the same speed, but for a given gas at a given temperature, the *average* velocity is the same in all samples regardless of the pressure.

5. At a given temperature, the molecules of different kinds of gases have the same average kinetic energy. An increase in mass is compensated for by a decrease in average velocity. That is, at a certain temperature,  $KE = 1/2 m_A v_A^2 = 1/2 m_B v_B^2 = \text{etc.}$  If  $m_A$  is greater than  $m_B$ , then  $v_A$  must be less than  $v_B$ .



In a sample of air, the abundant molecules are particles of nitrogen (diatomic molecules, N<sub>2</sub>) and oxygen (diatomic molecules, O<sub>2</sub>), with lesser amounts of argon (monatomic molecules, Ar), water (triatomic molecules, H<sub>2</sub>O), and carbon dioxide (triatomic molecules, CO<sub>2</sub>).

FIG. 7-1

**Individual Particles in Gases.** The individual particles normally present in a gaseous substance are called molecules (Fig. 7-1). In the special case of the noble gases—helium, neon, argon, krypton, xenon, and radon—the individual particles are single atoms, but they are still called molecules or, to emphasize their atomic character, *monatomic* molecules.

In addition to the noble elements, there are a few other elements that are gases at room temperature. These are hydrogen, nitrogen, oxygen, fluorine, and chlorine. As pointed out in Chap. 5, the individual particles of these elements in the gaseous state are not single atoms, but diatomic molecules, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, F<sub>2</sub>, and Cl<sub>2</sub>, respectively.

## PRESSURE OF GASES

**Measurement of Gas Pressure.** Torricelli, a student of Galileo, made the first instrument for measuring the pressure of the atmosphere. One procedure that he employed was to fill a glass tube with mercury and then invert it in a dish of mercury (Fig. 7-2). If the tube was long enough, he found that the mercury would fall away from the upper end of the tube. Torricelli considered the empty space above the mercury a vacuum, but today we know this space is not completely free of particles. Although it is very nearly a perfect

A Torricelli barometer made by inverting a long tube of mercury and placing it in a dish of mercury (left). A simple manometer for measuring low pressures is shown on the right. Since the tube is short, the air pressure keeps the mercury pushed to the top of the tube. When this manometer is connected to a low pressure system (see Fig. 7-3), part of the mercury moves into the left limb, and the difference in height of the two levels is a measure of the pressure.

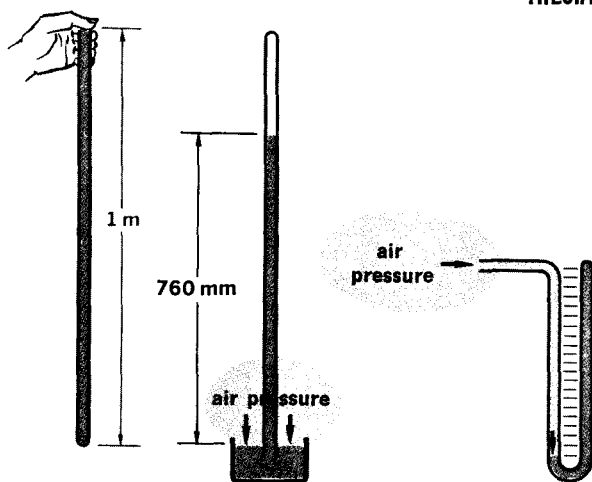


FIG. 7-2

vacuum, it does contain a small number of mercury molecules (mercury vapor). Such inverted tubes are **barometers**; the height of the mercury is determined by the pressure of the atmosphere. Like Torricelli, we can think of the atmosphere as a "sea of gas" that presses on objects just as a sea of water presses on objects beneath its surface. The level in the barometer changes continuously, rising as the atmospheric pressure increases, falling as the atmospheric pressure decreases. The highest and lowest readings during a year may differ by as much as 30 to 40 mm in a given locality.

In addition to the regular changes in pressure due to changing weather conditions, changes in altitude also affect the height of the barometer. At sea level, the average height is near 760 mm; on the top of Mount Whitney, in California, the mercury in a barometer would rise to only about 450 mm. The average pressure at sea level is taken as the **standard atmospheric pressure**. It is expressed in several ways: 14.7 psi, 760 mm of mercury, or simply 1 atmosphere (atm). Figures 7-3 and 7-4 show two common methods of measuring gas pressure in laboratory work.

## BOYLE'S LAW

The behavior of air revealed by experiments similar to those shown schematically in Fig. 7-5 is typical of all gases. At any constant temperature, the greater the pressure on a sample of gas, the less the volume. Since all gases act in this way, this behavior is called a *law of nature*. First demonstrated in about 1660 by the Englishman Robert Boyle, it is known as **Boyle's law**. *If the temperature remains constant, the volume of a given amount of gas varies inversely with the pressure.*

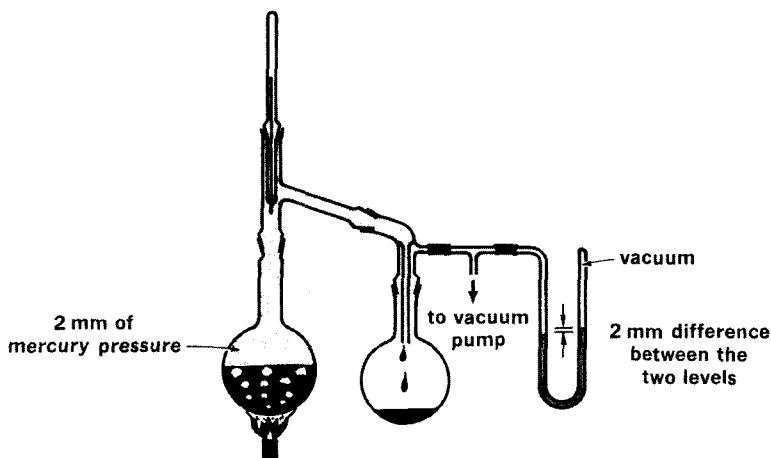


FIG. 7-3

By lowering the pressure to a few millimeters, the boiling point of a substance may be lowered by as much as a hundred degrees. (For example, water boils at  $100^{\circ}\text{C}$  at 760 mm and at  $0^{\circ}\text{C}$  at 4 mm.) Distillation of an unstable substance may then take place without decomposition. A manometer is used in the distillation system to make sure that the pressure is kept at the desired minimum.

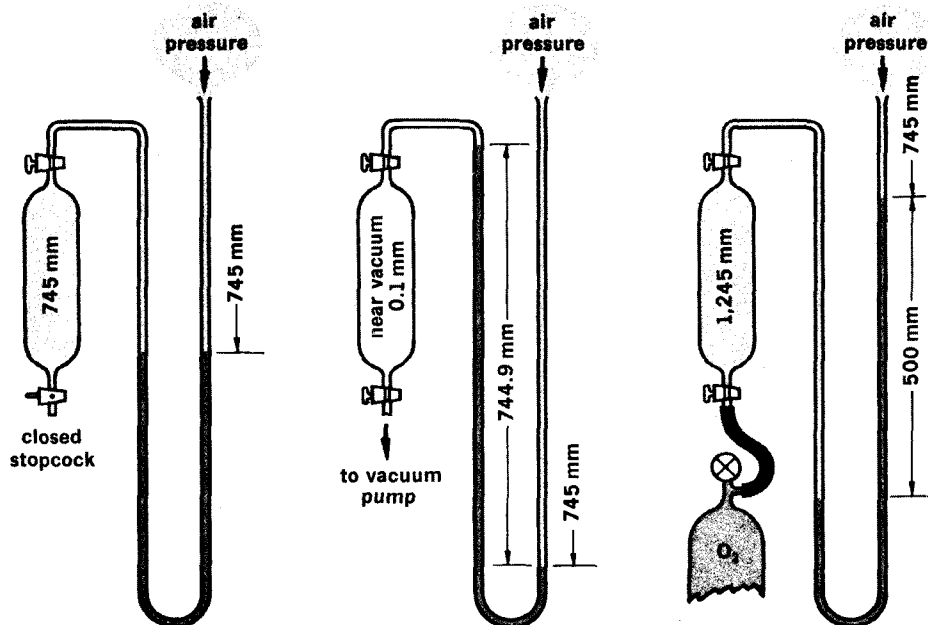


FIG. 7-4

Illustrating the use of manometers to measure gas pressure. The gas pressure in the flask at the left equals that of the atmosphere. For the flask in the center, the position of the mercury shows that almost all of the gas has been pumped out of the flask. At the right, the flask has been filled with oxygen to a pressure of 1245 mm, that is, the sum of the pressure indicated by the height of the mercury column (500 mm) and the air pressure (745 mm).

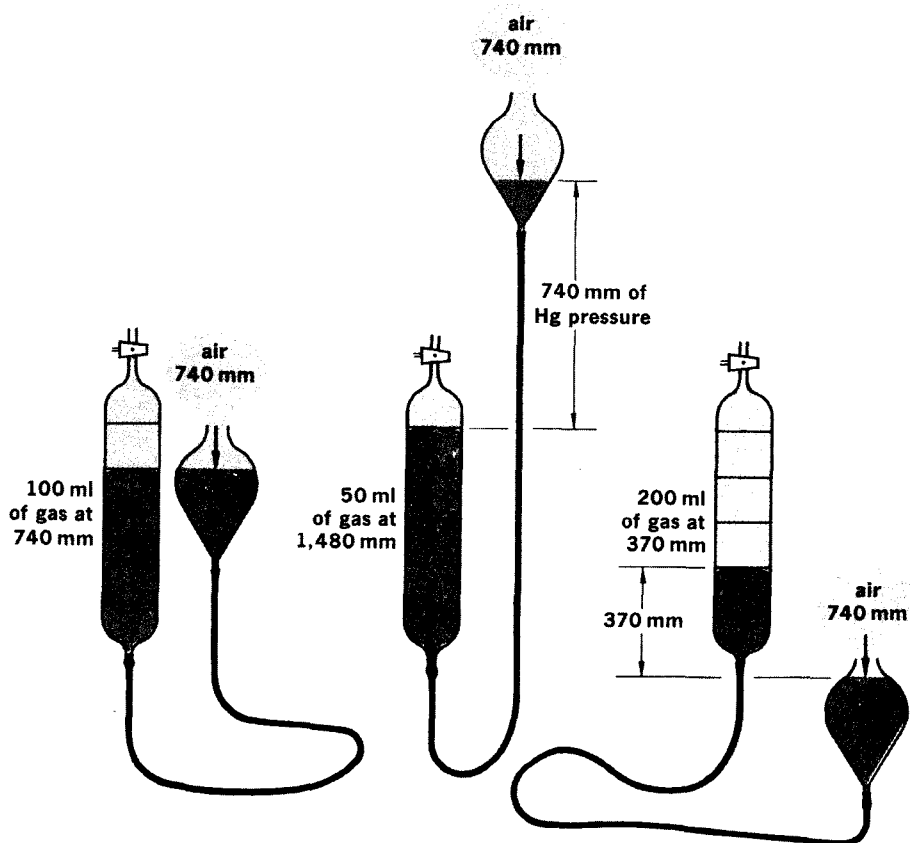


FIG. 7-5

Illustration of Boyle's law. When the mercury bulb is raised to a position so that the pressure is doubled (middle), the volume of the trapped gas becomes one-half of the original value; when the mercury is lowered (right) so that the pressure is halved, the volume becomes twice the original value.

The kinetic theory very nicely explains the fact that the pressure exerted by a given mass of gas increases as the volume decreases. According to this theory, the particles are moving at the same speed (the temperature is not changed). But they strike the sides of the container more often, because they do not have so far to go before striking either a neighbor or the container. Thus, if a given volume of gas is compressed so that the volume is reduced to one-half, the molecules collide with one another and with the walls of the container twice as often. This means that the pressure exerted by the gas is doubled. If the volume is again reduced by one-half, the crowded condition of the molecules again results in twice as many collisions, and the pressure again doubles.

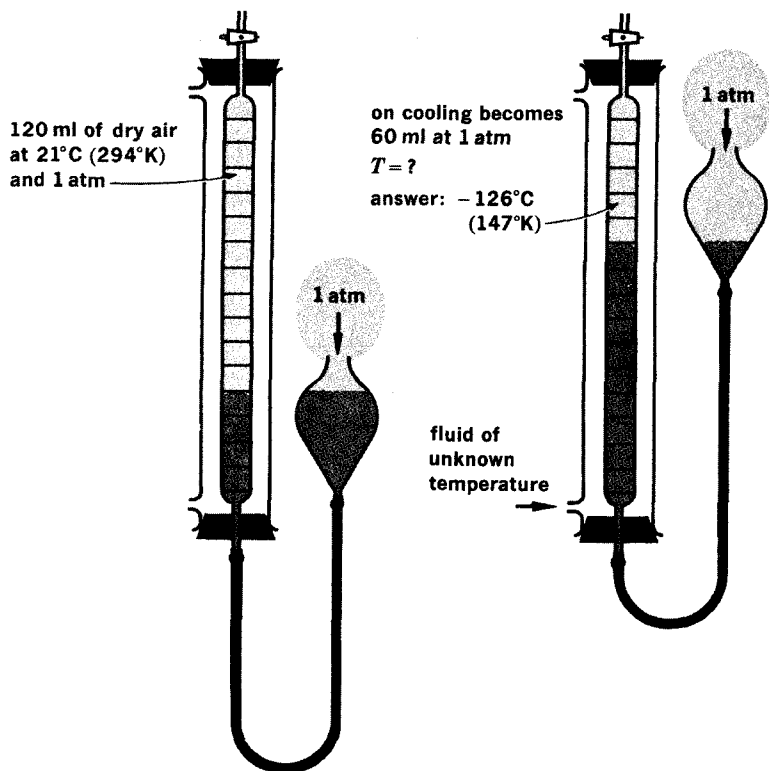


FIG. 7-6

A gas thermometer interpreted on the basis of Charles' law. The volume of a quantity of dry air is measured at a known temperature and at the temperature to be measured. The pressure must be kept constant during the measurements by raising or lowering a bulb of liquid so that the pressure of the gas is always the pressure of the atmosphere. In the example illustrated here, the unknown temperature is:  $(273 + 21)^{\circ}\text{K} \times 60/120 = 147^{\circ}\text{K}$ ;  $147^{\circ} - 273^{\circ} = -126^{\circ}\text{C}$ . (The confining liquid in the case illustrated here cannot be mercury. Why?)

### CHARLES' LAW

If a certain quantity of gas is confined at constant pressure in a vessel, the volume of the gas changes with the temperature. Figure 7-6 is a diagram of an apparatus used to demonstrate this effect. Gas is trapped above mercury in a graduated tube encased in a jacket through which fluid at a desired temperature can be circulated. When the temperature increases, the volume of the gas increases, and vice versa. By raising and lowering the leveling bulb, the level of the mercury inside the tube is kept equal to the level in the bulb; in this way the pressure of the trapped gas can be kept constantly equal to the pressure of the atmosphere. By properly positioning the leveling bulb, a chosen constant pressure above or below atmospheric pressure can be maintained.

Suppose a tube like the one shown in Fig. 7-6 contains 100 ml of dry air at  $0^{\circ}\text{C}$ . Table 7-1 gives the volumes that the air would have at various other temperatures. Some liquid other than mercury would have to be used to confine the air below  $-38.87^{\circ}\text{C}$ , the freezing point of mercury; also, above about  $100^{\circ}\text{C}$  the evaporation of the mercury would begin to add appreciably to the volume of trapped gas.

*Change in volume of air with temperature*

TABLE 7-1

temperature, $^{\circ}\text{C}$	volume, ml	temperature, $^{\circ}\text{C}$	volume, ml	temperature, $^{\circ}\text{C}$	volume, ml
273	200	100	137	- 50	82
200	173	50	118	-100	63
150	155	0	100	-150	45

The data from Table 7-1 are plotted in the graph in Fig. 7-7. The straight-line relationship of temperature-volume shows that the *changes* in volume of a gas are directly proportional to the *changes* in temperature. First recognized about 1787 by the French scientist Jacques Charles, this law of gases was stated in a general way by J. L. Gay-Lussac in 1802.

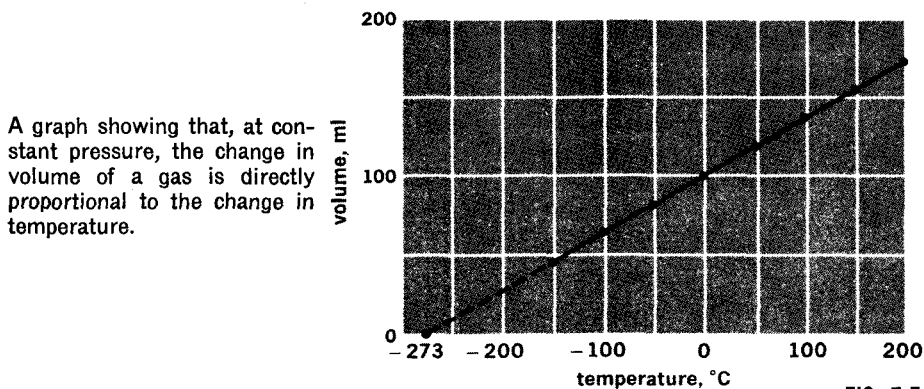


FIG. 7-7

**Absolute Scale of Temperature.** Extrapolation of the straight line in Fig. 7-7 leads to the idea that, if the temperature were lowered enough, to  $-273^{\circ}\text{C}$ , the volume of the air would fall to zero. But it is inconceivable to think that matter can ever have a volume of zero. It is believed, however, that the kinetic energy of all molecules (or ions or atoms) becomes zero at  $-273^{\circ}\text{C}$  (more precisely,  $-273.15^{\circ}\text{C}$ ).

Is there a lowest temperature? Is there a highest temperature?

The lowest possible temperature is that at which the kinetic energy of molecules is zero. Since  $KE = \frac{1}{2} mv^2$ , this is the temperature at which velocity = 0, the temperature at which no molecule can move. This temperature, calculated to be  $273.15^\circ$  below centigrade zero, has been named *absolute zero* and has been taken as the starting point of the absolute temperature scale. Although a simple extrapolation like that shown in Fig. 7-7 indicates that an absolute zero temperature exists, it was not till 1848 that Lord Kelvin convincingly demonstrated the validity of the absolute scale of temperature. On the **Kelvin scale**, absolute zero is designated as  $0^\circ K$ . A change of  $1^\circ K$  is equal in magnitude to a change of  $1^\circ C$ , so that the freezing point of water, which is  $273.15^\circ$  above absolute zero, has the value of  $273.15^\circ K$  on the Kelvin scale. *To convert  $^\circ C$  to  $^\circ K$ ,  $273^\circ$  (more precisely,  $273.15^\circ$ ) is added to the centigrade temperature.*

The highest temperature possible has not been calculated. The temperature inside the sun is estimated at  $30,000,000^\circ K$ ; the temperature attained in a hydrogen-bomb blast is estimated at  $100,000,000^\circ K$ . It is interesting to note that the environment we live in is quite chilly in terms of the lowest and the highest temperatures.

**Statement of Charles' Law.** In Fig. 7-7 the straight-line graph of the temperature of a gas versus its volume shows that *changes* in these quantities are directly proportional to each other. However, no direct ratio exists between volume and temperature if the temperature values are taken from the centigrade or Fahrenheit scales. The numbers on these scales are relative values only. Neither  $0^\circ C$  nor  $0^\circ F$  signifies a complete lack of temperature, because on both scales we can read temperatures "below zero."

Because it is only on the absolute scale that  $0^\circ$  means no temperature, any statement of a direct ratio between volume and temperature must mention that absolute values are being used. *If the pressure does not change, the volume of a given quantity of gas is directly proportional to the absolute temperature.* This is known as **Charles' law**.

## LIQUEFACTION OF GASES

According to the kinetic theory, the molecules in a gas are attracted to one another by van der Waals forces. Because of the high velocity of the gas molecules at ordinary temperatures and the distance between them, these weak attractive forces are not able to pull the molecules together. If the kinetic energy of the gas molecules is lowered by decreasing the temperature, the van der Waals forces can finally pull the particles close to one another and hold them together in the liquid state. The strength of these forces is inversely proportional to a high power of the distance between the molecules. If the molecules are far apart, the attraction is weak; but as they

come close to one another, the attraction increases. When an increase in pressure crowds the molecules more closely together, the gas liquefies if the attractive forces are great enough.

However, there is a minimum temperature for each gaseous substance above which the gas cannot be liquefied no matter how much pressure is applied. This temperature is called the **critical temperature**. The pressure that must be applied to bring about liquefaction when a gas is at its critical temperature is called the **critical pressure**. The nonpolar molecules of such gases as hydrogen, oxygen, and nitrogen have relatively small attraction for one another. The kinetic energy of molecules of these gases must be decreased a great deal before the slight attractive forces (made more effective by the application of pressure) can hold them in the liquid form. Their critical temperatures are quite low (Table 7-2). On the other hand, polar molecules of such gases as ammonia and sulfur dioxide have relatively great attraction for one another, great enough to hold them in the liquid state at temperatures well above room temperature if sufficient pressure is applied.

*Critical temperatures and pressures*

TABLE 7-2

gas	boiling point, °C	critical temperature, °C	critical pressure, atm
hydrogen	-252.8	-239.9	12.8
nitrogen	-195.8	-147.1	33.5
oxygen	-183.0	-118.8	49.7
methane	-161.5	- 82.5	45.8
ammonia	- 33.3	132.4	111.5
sulfur dioxide	- 10.0	157.2	77.7
water	100.0	374.0	217.7

A gas cannot be liquefied at a temperature above its critical temperature; it can be liquefied at a temperature below its critical temperature; the lower the temperature, the less the pressure required to bring about liquefaction.

## LIQUID STATE

The early theory of molecules in motion was based largely on the experimental study of gases, but it applies with slight modifications to liquids and solids. The material that follows is arranged in a fact-theory scheme to emphasize that the theory is based on simple experimental evidence.

**Compressibility. Fact:** Liquids are compressed only under extremely high pressures. The fact that liquids are almost incom-



pressible leads to their use in hydraulic brake systems. Pressure exerted on the brake fluid causes the brake to move, since the volume of the fluid is not reduced by the pressure.

*Theory:* The particles in a liquid are not widely separated; rather, they touch one another. The liquids cannot be compressed much by crowding the particles together, but only by squeezing and deforming the molecules themselves. This requires tremendous pressure.

*Diffusion. Fact:* Colored solutions diffuse through water. Diffusion is much slower in a liquid than in a gas, but it takes place at an easily measured rate. One liquid may diffuse through another, or a solid may dissolve and diffuse through a liquid. Diffusion is hastened by stirring.

*Theory:* The molecules do not move about so freely as gas molecules, but they move at all times and slide over one another without much difficulty. They are attracted to one another, but not rigidly held together.

*Evaporation and Solidification. Fact:* When the temperature of a liquid is raised, it evaporates more quickly. If its temperature is lowered sufficiently, the liquid freezes to a solid.

*Theory:* The energy of the moving particles in a liquid is increased by a rise in temperature. When the molecules have enough kinetic energy, they break away from their neighbors and become gas molecules. A fall in temperature means a decrease in the energy of the moving molecules. If the kinetic energy of the molecules falls enough, even weak van der Waals forces are able to hold the particles together in the fixed positions of a solid.

*COOLING EFFECT OF EVAPORATION. Fact:* When a liquid evaporates, the liquid left behind, or the surface from which the evaporation occurs, tends to be cooler.

*Theory:* In evaporation, the molecules that escape are the ones with the greatest velocity. The average velocity and the average kinetic energy of the molecules left in the liquid are reduced as evaporation proceeds. Because molecular motion is heat, the quantity of heat energy for a given number of molecules is also reduced, and so is temperature. Evaporation always results, therefore, in cooling effects. Unless the evaporating liquid is completely insulated, heat is absorbed from the surroundings and the process continues till the liquid evaporates completely.

*Individual Particles in Liquids.* Pure substances that exist as liquids at room temperature usually consist of (covalent) molecules containing more than one atom. Mercury is the most common member of the small class of liquids that are composed of atoms (monatomic molecules). In electrovalent compounds, the bonds between the ions lead to the formation of solids that have high melting points.

## VAPORIZATION

Liquids that evaporate readily consist of molecules which are slightly cohesive (van der Waals forces) but which tend to scatter because of their own motion. As shown in Fig. 7-8, some molecules

When the rate of evaporation equals the rate of condensation, the liquid and vapor are in equilibrium.



FIG. 7-8

escape from the body of the liquid (vaporize) if they happen to be headed upward with sufficient velocity to overcome the weak attractive forces. *Vapor* is the name given to gaseous molecules of a substance at a temperature and pressure that would ordinarily lead us to think of the substance as a liquid or solid. Molecules of a vapor are usually diffused into another gas, such as air. A liquid that evaporates readily is said to be volatile. Ether is a very volatile liquid; lubricating oil is only slightly volatile.

**Vapor Pressure.** Water escapes from a vessel by evaporation only if the vessel is open. If the vessel is closed, does evaporation cease? Of course not; as Fig. 7-8 shows, the molecules that escape from the surface of the liquid are trapped in the container. As they collide with one another and the walls of the container, they may hit the surface of the liquid and rejoin it. The bottle of water shown in Fig. 7-8 represents a system in which the liquid is evaporating and the vapor condensing at the same rate. When the rate of evaporation equals the rate of condensation, the system is in *equilibrium*. The **vapor pressure** of a substance is defined as the pressure exerted by the gas of that substance when it is in equilibrium with the liquid or solid phase. The vapor pressures of liquids (or solids) increase as the temperature increases. Figure 7-9 shows one method of determining the vapor pressure of a liquid.

In Fig. 7-10 the data for the changes in vapor pressure due to temperature for four liquids are plotted.

**Boiling.** The **boiling point** of a liquid is the temperature at which the pressure of the vapor escaping from the liquid equals the outside pressure. When the vapor pressure equals the outside (or applied) pressure, bubbles begin to form throughout the liquid and it boils. The **normal boiling point** of a liquid is defined as the temperature at which its vapor pressure is 760 mm, that is, standard atmospheric pressure.

The boiling point of water (and other liquids) varies with the atmospheric pressure. In mountainous regions the boiling point of water is considerably below  $100^{\circ}\text{C}$ , because the atmospheric pressure is below 760 mm (Table 7-3).

At high altitudes housewives must boil foods longer because of

# STATES OF MATTER; KINETIC THEORY

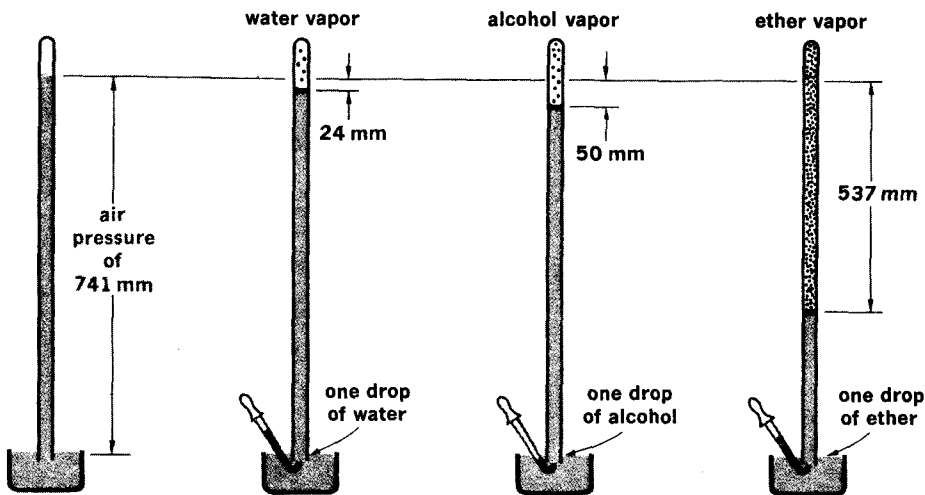
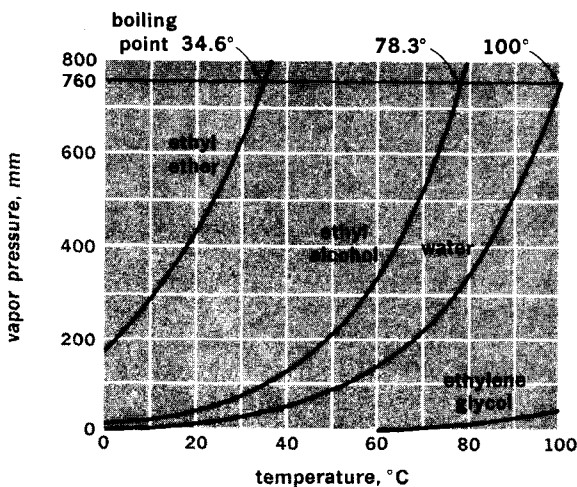


FIG. 7-9

The use of Torricellian barometers to determine the vapor pressures of liquids. As shown in the diagram, when a drop of a liquid is introduced into a barometer it rises to the top of the mercury column and evaporates. The space above the mercury quickly becomes saturated, that is, an equilibrium is established between the liquid and vapor phases of the sample. The pressure exerted by the vapor forces the mercury column to fall. The fall in the height of the column is a direct measure of the vapor pressure. The barometer at the left has a Torricellian vacuum above the mercury. Into each of the other three barometers, a drop of a liquid has been placed: from left to right, drops of water, ethyl alcohol, and ethyl ether. The temperature is 25°C.



A plot showing the effect of temperature on the vapor pressures of four common liquids. The temperature at which the vapor pressure is 760 mm is the normal boiling point of the liquid.

FIG. 7-10

the low boiling temperatures. Conversely, foods cook more rapidly in pressure cookers, because they can be heated above the normal

boiling point. For example, a pressure of 10 psi over the standard atmospheric pressure permits water to boil at about 115°C.

### *Changes in boiling point of water with altitude*

TABLE 7-3

	altitude, ft	average atmospheric pressure, mm	boiling point of water, °C
sea level	0	760	100
Mt. Mitchell	6,684	589	93
Mt. Whitney	14,495	451	86
Mt. Everest	29,141	244	71

## SOLID STATE

**Compressibility. Fact:** It is even more difficult to compress solids than liquids.

**Theory:** The particles that make up solids are in contact with one another. Any significant compression must result in the deforming of the individual particles.

**Diffusion. Fact:** It is not widely known that diffusion can take place even in a solid body, but this process can be demonstrated in a relatively simple way. If a polished flat piece of pure zinc and a polished flat piece of pure copper are clamped together for a considerable time, say a year, some zinc penetrates the copper, and vice versa (Fig. 7-11).

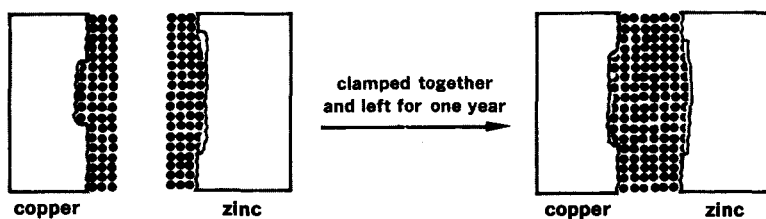


FIG. 7-11

Diffusion of atoms, ions, or molecules can take place even in solids. The diffusion of zinc and copper atoms is shown schematically here.

**Theory:** Movement of the particles in a solid is very limited, but some movement is possible.

**Melting. Fact:** When a solid is heated, it usually melts to a liquid.

**Theory:** A rise in temperature brings about an increase in the kinetic energy of the particles. If the molecular motion increases sufficiently, the attractive forces are largely overcome, so that the particles are no longer held in fixed positions. They slip and slide over one another and display the usual characteristics of a liquid.

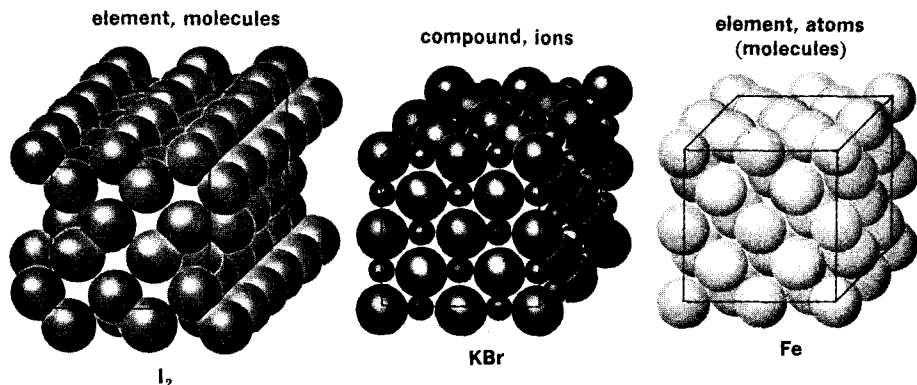


FIG. 7-12 A solid may be considered a collection of molecules, or ions, or atoms, depending on the nature of the substance.

**Sublimation.** Some solids, such as naphthalene (moth balls), and snow or ice below  $0^{\circ}\text{C}$ , may pass directly from the solid state to the vapor state. The reverse process, deposition directly from the vapor state to the solid state, is also quite common. *Sublimation* is the process of passing from a solid state to the gaseous state without going through the liquid state, or the passing from the gaseous state directly to the solid state.<sup>1</sup> An increase in temperature increases the rate of sublimation.

**Individual Particles in Solids.** Pure substances that exist as solids at room temperature may consist of ions, molecules, or atoms, as shown in Fig. 7-12. Most elements that are solids at room temperature are considered to consist of atoms, although these atoms may be different from isolated single atoms because of their chemical union with one another (see metallic bond, page 458). For example, the symbols for iron, tin, zinc, copper, and gold are written simply as Fe, Sn, Zn, Cu, and Au, respectively. The symbol without any subscript refers to a single atom.

All strictly ionic compounds are solids at room temperature. This is due to the fact that the ions arrange themselves in certain three-dimensional patterns or crystal forms, in which positive and negative ions alternate. No definite molecules are formed, but the forces of attraction between the unlike charges are so great that the ions are held rather rigidly in place. They probably vibrate, but movement from place to place is difficult. The ionic crystal extends out indefinitely till it is broken or stops growing (it can be considered to be a single huge molecule of indefinite size).

<sup>1</sup> Although the same word has been used for years for both processes, it has been suggested that two terms should be used: *sublimation* for solid  $\rightarrow$  gas and *deposition* for gas  $\rightarrow$  solid.

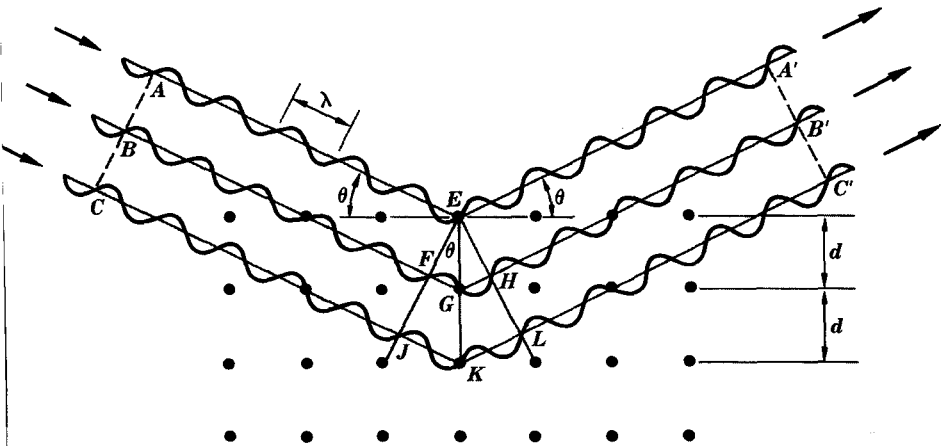
## CRYSTALLINE SOLIDS

Crystals are solid bodies bounded by planar surfaces. Because many solids such as rock salt, quartz, and snowflakes exist in forms that are obviously symmetrical, scientists long suspected that the atoms, ions, or molecules of these solids were also arranged symmetrically.

**X-ray Studies.** In 1912, the German physicist Max von Laue suggested that, if X rays were a type of electromagnetic radiation like light, the wavelengths of the X rays should be of the proper length to be diffracted by atoms or ions in a crystal lattice. Experimental tests of this hypothesis showed that an X ray did behave as electromagnetic radiation of short wavelength. This discovery opened a new field of research in measuring distances between planes of atoms and ions and made possible the calculation of the sizes and arrangements of these small particles.

The simplest case to consider is that in which the X radiation has a single wavelength, that is, the radiation is monochromatic. When a monochromatic beam of X rays falls on a crystalline substance, the radiation is strongly diffracted only when the crystal is turned at certain angles to the incident beam. Two English physicists, the father and son team of W. H. and W. L. Bragg, showed that the X ray can be thought of as being reflected at certain angles and that these angles are related to the wavelength of the X rays and to the distances between the parallel planes of atoms or ions in the crystal.

In Fig. 7-13 a schematic representation of the relationship discovered by the Braggs is shown. When the X rays are efficiently



Schematic representation of the diffraction of a beam of X radiation of wavelength  $\lambda$  at the angle  $\theta$  by a crystal made of planes of atoms whose centers are separated by the distance  $d$ .

FIG. 7-13

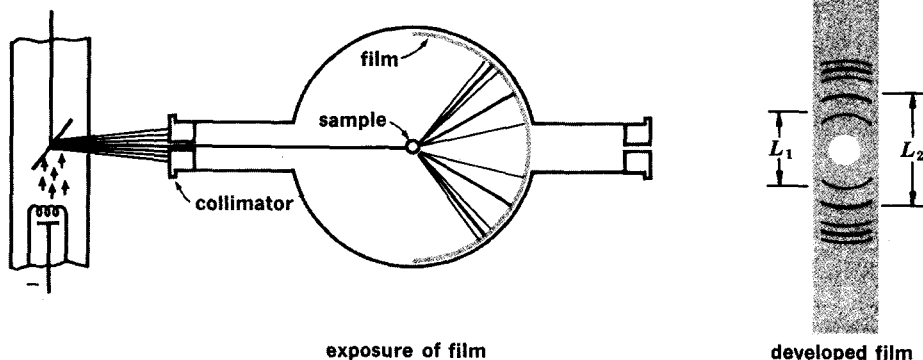


FIG. 7-14

X-ray diffraction camera used with powdered sample. The many minute crystals diffract the pin-point X ray in conical envelopes at various angles; the developed film reveals a pattern of lines which show where the various cones strike the film. By measuring distances between pairs of lines on the film, for example,  $L_1$  or  $L_2$ , and the diameter of the camera, the angles of diffraction  $\theta$  (see Fig. 7-13) can be determined. The angle between a pair of lines is  $4\theta$ , where  $\theta$  is the angle used in the Bragg equation.

reflected, the waves that are in phase at  $ABC$  reach  $A'B'C'$  in phase. This is possible only if the differences in the distances  $AEA'$ ,  $BGB'$ , and  $CKC'$  are whole-number multiples of the wavelength  $\lambda$ . In the figure, the difference between the distances represented by  $AEA'$  and  $BGB'$  is  $FGH$ , a distance of  $1\lambda$ . The difference between  $AEA'$  and  $CKC'$  is  $JKL$ , a distance of  $2\lambda$ .

In Fig. 7-13, we see that for the right triangle  $EFG$  the sine of angle  $\theta$  is  $FG/EG$  (the length of the side opposite  $\theta$  divided by the hypotenuse). But  $EG$  equals  $d$ , the distance between planes; and  $FG$  is  $\frac{1}{2}\lambda$  in our drawing. So,

$$\sin \theta = \frac{FG}{EG} = \frac{\frac{1}{2}\lambda}{d} \quad \text{or} \quad \lambda = 2d \sin \theta$$

For the general case, it is only necessary that the distance  $FGH$  be a whole number multiple,  $n$ , of the wavelength, so that the Bragg equation becomes

$$n\lambda = 2d \sin \theta$$

One application of the Bragg equation is the calculation of  $d$  values for a crystalline solid. It is necessary that  $\lambda$  be known and that values of  $\theta$  be precisely measured. One method of measuring the angles of reflection is with an X-ray camera such as that in Fig. 7-14. A small sample of powdered crystals of a sample  $S$  is slowly rotated and irradiated with a beam of X rays. The beam is reflected at certain angles and gives rise to a pattern of lines on a strip of photographic film  $F$ . The X-ray powder pattern of a substance may consist of perhaps 10 to more than 100 pairs of lines of various

intensities and spacings. The pattern for a substance is practically unique for purposes of identification; even mixtures of substances can be analyzed if they are not too complex. Patterns of thousands of compounds have been determined and recorded in the chemical literature.

**CALCULATION OF IONIC RADII.** Consider the following data obtained for the X radiation of potassium bromide.

wavelength of X ray emitted by tube with a copper anode	1.5412 Å
diameter of X-ray camera	71.62 mm
distance on film between the most intense pair of lines	33.85 mm
angle $\theta$ calculated	13.54°
$\sin \theta$ , from handbook	0.2340
interplanar distance $d$ calculated from Bragg equation (with $n = 1$ ), $d = \frac{1.5412 \text{ Å}}{2(0.2340)} =$	3.29 Å

The distance between the second most intense pair of lines is 48.30 mm, from which a  $d$  value of 2.33 Å is calculated. Figure 7-15 shows how these two distances are assumed to be related in a crystal of potassium bromide. Many other families of planes can be drawn; the  $d$  values for these planes can be calculated from other less intense lines in the KBr film pattern.

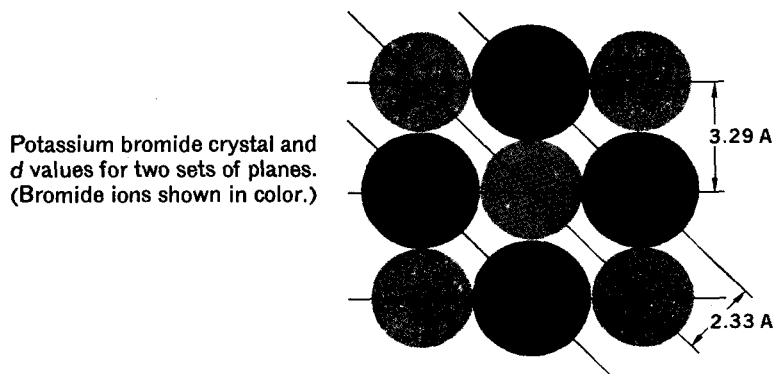


FIG. 7-15

The obvious question is: How much of the 3.29 Å distance in KBr is due to the radius of the K⁺ ion and how much to the Br⁻ ion? Individual ionic radii have been calculated on the basis of X-ray patterns for many compounds, for example, KF, KCl, KBr, KI, LiBr, NaBr, RbBr, and CsBr. The calculated radii of K⁺ or Br⁻ or other ions varies slightly from compound to compound but a consistent set of "best values" can be chosen. The accepted values of K⁺, 1.33, and Br⁻, 1.95 Å, agree well with the interplanar distance of 3.29 Å for potassium bromide.



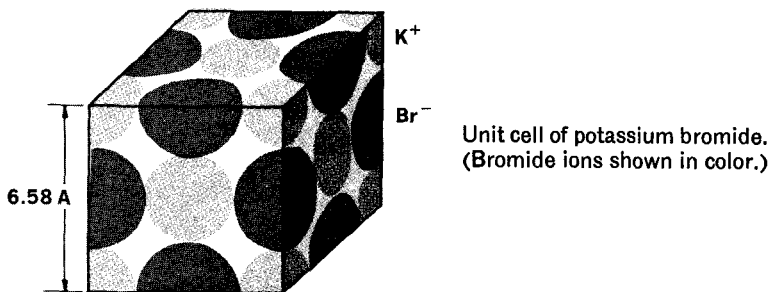


FIG. 7-16

**CALCULATION OF AVOGADRO'S NUMBER.** X-ray measurements can be used to calculate the number of atoms (or molecules or pairs of ions) in a mole. Consider the unit cell of potassium bromide drawn in Fig. 7-16. From the dimensions of the cell we calculate that 4 K<sup>+</sup> ions and 4 Br<sup>-</sup> ions occupy a volume of 285 Å<sup>3</sup>. From a handbook we find the density of KBr to be 2.75 g/cm<sup>3</sup> at 25°C:

$$\begin{aligned} \text{no. K}^+, \text{Br}^- \text{ pairs per mole} &= \left( \frac{4 \text{ pairs}}{285 \text{ Å}^3} \right) \left( \frac{1 \times 10^8 \text{ Å}}{1 \text{ cm}} \right)^3 \left( \frac{1 \text{ cm}^3}{2.75 \text{ g}} \right) \left( \frac{119.0 \text{ g}}{1 \text{ mole}} \right) \\ &= 6.07 \times 10^{23} \text{ pairs of ions per mole} \end{aligned}$$

More precise X-ray and density measurements enable one to calculate Avogadro's number more precisely.

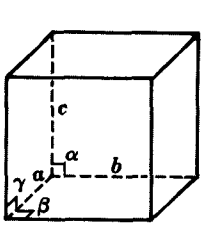
**Types of Crystals.** The individual particles in most solids are arranged in beautifully symmetrical patterns called crystal structures. There are six fundamentally different crystal arrangements. These are the *isometric* (for example, cubic), *tetragonal*, *monoclinic*, *triclinic*, *orthorhombic*, and *hexagonal*. They are sketched in Fig. 7-17.

The *isometric* arrangement includes some of the simple crystal forms characteristic of many common and important substances. Among these forms are the *cube*, the *tetrahedron*, and the *octahedron*. Figure 7-18 shows the relation of these three figures to one another. A cube could be called a *hexahedron*, that is, *six* sides; a *tetrahedron* has *four* sides (it is the simplest solid figure); an *octahedron* has *eight* sides.

There are several ways of representing a crystal structure by means of a drawing. Consider sodium chloride, NaCl. X-ray experiments show that this compound crystallizes in a modified cubic pattern, in which the closest neighbor of any sodium ion is a chloride ion, and vice versa. In Fig. 7-19 this structure is drawn in three ways.

Figure 7-19a indicates the position of the centers of the ions by means of the points of intersection of the lines. It gives only a general idea of the cubic nature of the crystal.

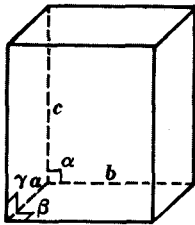
Figure 7-19b identifies the Na<sup>+</sup> and Cl<sup>-</sup> ions. The small circles show only the position of the centers of the ions. From a study of this figure we can see that every Na<sup>+</sup> ion has six Cl<sup>-</sup> ions as its near-



**cubic**

$$a = b = c;$$

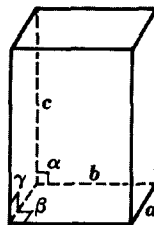
$$\alpha = \beta = \gamma = 90^\circ$$



**tetragonal**

$$a = b \neq c;$$

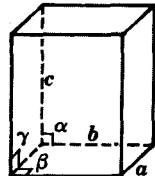
$$\alpha = \beta = \gamma = 90^\circ$$



**monoclinic**

$$a \neq b \neq c;$$

$$\alpha \neq 90^\circ; \beta = \gamma = 90^\circ$$

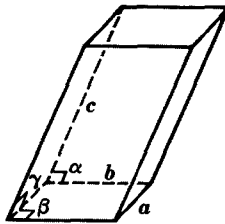


**orthorhombic**

$$a \neq b \neq c;$$

$$\alpha = \beta = \gamma = 90^\circ$$

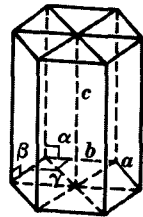
Six different crystal arrangements. The three crystal axes are designated  $a$ ,  $b$ , and  $c$ , and the angles between the axes are designated  $\alpha$ ,  $\beta$ , and  $\gamma$ . (Redrawn by permission from Therald Moeller, *Inorganic Chemistry*, John Wiley & Sons, Inc., 1952.)



**triclinic**

$$a \neq b \neq c;$$

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



**hexagonal**

$$a = b \neq c;$$

$$\alpha = \beta = 90^\circ;$$

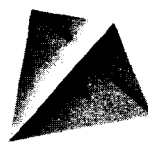
$$\gamma = 120^\circ$$

FIG. 7-17

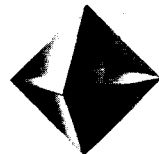
Three of the most common crystal forms of solid substances.



**cube**  
6 faces

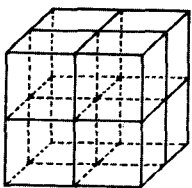


**tetrahedron**  
4 faces

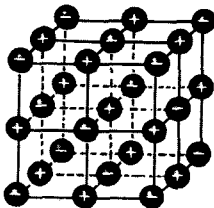


**octahedron**  
8 faces

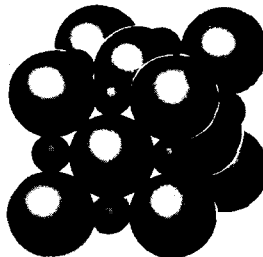
FIG. 7-18



(a)



(b)



(c)

FIG. 7-19

Three ways of representing the structure of sodium chloride. The positive sodium ions are smaller than the negative chloride ions.

est neighbors, and that every  $\text{Cl}^-$  ion has six  $\text{Na}^+$  ions as its nearest neighbors. A sodium ion may be thought of as being in the center of an octahedron bounded by the six chlorine ions.

Figure 7-19c not only identifies the ions and shows their position but gives an idea of their relative sizes. It indicates two other important things: (1) the ions are touching one another so as to take up practically all the space; (2) these ions may be spherical (like marbles), and consequently, when they pack together, small empty spaces are left.

Each of these drawings has a special significance. The third one is the most easily understood, but the second or even the first may be more effective in describing a complicated crystal.

**Isomorphism.** From the Greek word *morphē*, meaning form, is derived the word ending *-morphous*. Two substances which have the same crystal form and which crystallize together in all proportions are said to be **isomorphous**. The formulas of a pair of such substances usually reveal that their atoms are in the same ratios. Examples are:

$\text{K}_2\text{SO}_4$ and $\text{K}_2\text{SeO}_4$	2 : 1 : 4
$\text{NaNO}_3$ and $\text{CaCO}_3$	1 : 1 : 3
$\text{NaF}$ and $\text{MgO}$	1 : 1
$\text{Cr}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$	2 : 3

Isomorphous substances crystallize together in homogeneous mixtures. However, similarity of both formula and chemical properties is not enough to insure homogeneous crystallization. A famous pair of similar substances that does not crystallize homogeneously is  $\text{NaCl}$  and  $\text{KCl}$ .

A single substance that crystallizes in two or more different forms, under different conditions, is said to be **polymorphous** (many forms). Calcium carbonate,  $\text{CaCO}_3$ , silicon dioxide,  $\text{SiO}_2$ , sulfur, S, and carbon, C, are examples of polymorphous substances. In the case of elements, different crystalline forms have long been referred to as *allotropic* forms; for example, graphite and diamond are allotropic forms of carbon.

A substance that appears to be solid but has no well-developed crystal structure is said to be **amorphous** (without form). Tar and glass are such solids. Amorphous substances do not have sharp, definite melting points. Instead, they soften gradually as they are heated, and they melt over a range of temperature.

**Appearance of Crystals.** We must not jump to conclusions about the arrangement of the particles inside a large crystal from a consideration of its outer appearance. Because of limited space or for some other reason, a crystal may form by growing more in one direction than another.

Three habits which might be assumed by a substance that crystallizes in the cubic system. (Redrawn by permission from A. F. Wells, *Structural Inorganic Chemistry*, The Clarendon Press, Oxford, 1962.)

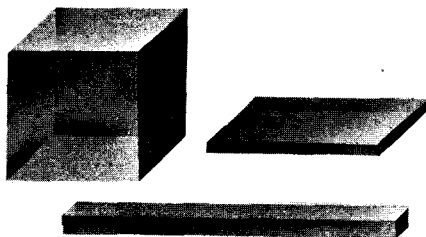


FIG. 7-20

Figure 7-20 shows a perfect cube along with two other shapes, a flat plate and a long needlelike structure. All three of these solids have the same crystal lattice, but their habits, or characteristic forms, differ. In Fig. 7-21 an octahedron is shown; also shown are three other possible habits that can be assumed by the octahedral system. One of these could be mistaken for a simple cube unless inspected closely.

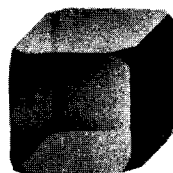
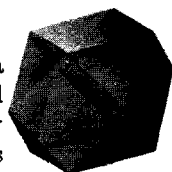
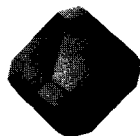
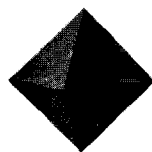


FIG. 7-21

Four habits which might be assumed by a substance that crystallizes in the octahedral system. (Redrawn by permission from A. F. Wells, *Structural Inorganic Chemistry*, The Clarendon Press, Oxford, 1962.)

**Melting (Fusion).** As the temperature of a crystalline solid rises, a temperature is reached at which it suddenly melts. If the liquid thus formed is cooled, we find that it freezes or solidifies at precisely the same temperature as that at which the solid melted (unless supercooling occurs). If solid and liquid phases of the same substance are in contact and the temperature is precisely at the melting point, the solid melts continually and the liquid freezes continually. When the rate of melting equals the rate of freezing, the system is said to be in equilibrium. The **melting point** of a substance is the temperature at which its solid and liquid phases are in equilibrium; if no heat is added or taken away, the weight of neither the solid nor the liquid changes (Fig. 7-22).

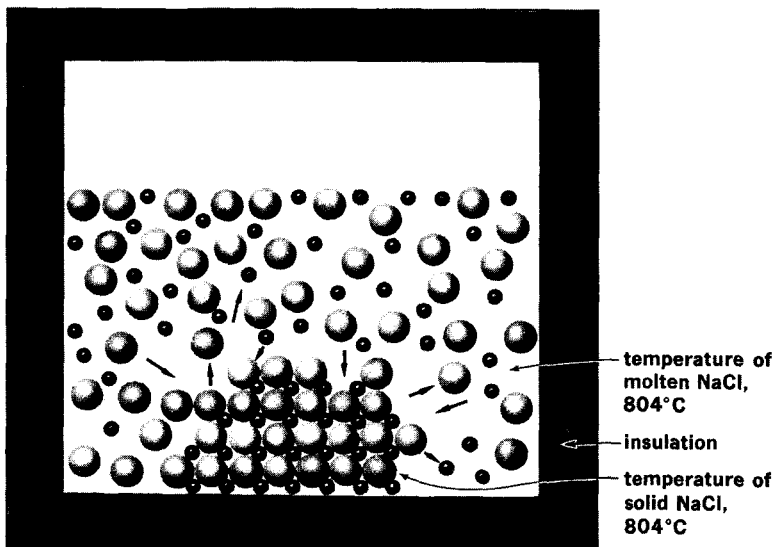
## ENERGY RELATIONSHIPS

### SPECIFIC HEAT

When a solid or a liquid or a gas is heated at a temperature other than the melting point or boiling point, the temperature of the substance increases.

In order to compare the effect of heat on the temperature of different substances, we measure the number of calories needed to change the temperature of one gram of the substance one degree

FIG. 7-22



Solid and liquid sodium chloride will remain together indefinitely at 804°C if no energy is allowed to enter or escape. However, individual ions leave the solid phase and enter the liquid phase; at the same time, other ions return from the liquid phase to the solid phase. Melting and crystallizing occur at the same rate, so that a dynamic equilibrium exists.

centigrade. This quantity of energy is called the specific heat. Table 1-2 lists the specific heat for a number of common substances.

Thus a given quantity of heat energy, say 10 cal, has more effect on the temperature of 5 g of gold than it does on the temperature of 5 g of water, because the specific heat of gold is lower.

A more general term than specific heat is heat capacity. The *heat capacity* is the quantity of heat required to increase the temperature of a substance by one degree. The **molar heat capacity** is the number of calories required to raise the temperature of one mole of a substance by one degree centigrade.

## HEAT OF FUSION

If 1 g of ice at  $-10^{\circ}\text{C}$  is carefully heated, we find that 0.478 cal is required for each  $1^{\circ}$  rise. Thus it takes  $(10)(0.478) = 4.78$  cal to bring the temperature to  $0^{\circ}\text{C}$ . As the gram of ice begins to melt, it is found that heat can be added without changing the temperature. In fact, 80 cal is required to change the gram of ice at  $0^{\circ}\text{C}$  to liquid water at  $0^{\circ}\text{C}$ . This heat energy is used in counteracting the attractive forces between molecules.

The number of calories needed to change one gram of a solid substance to one gram of liquid (at the melting point) is called the

heat of fusion. The heats of fusion for a number of substances are given in Table 7-4.

The same amount of heat is given up when a gram of a substance solidifies (*heat of solidification*) as is taken up when a gram of solid melts. For example, 80 cal is liberated to the surroundings when a gram of water freezes.

The heat required to melt one mole of a substance is called the molar heat of fusion or the *enthalpy of fusion*,  $\Delta H_{fus}$ . The enthalpy of fusion of ammonia,  $\text{NH}_3$ , at its melting point, as calculated from Table 7-4, is  $(17.0)(108.1)/1,000 = 1.84$  kcal/mole.

## HEAT OF VAPORIZATION

When 1 g of water at  $100^\circ\text{C}$  is vaporized, 540 cal of heat must be added to change this water to 1 g of steam. The temperature of the steam formed is  $100^\circ$ ; that is, the temperature is not increased at all. This 540 cal of heat energy is used in counteracting the attractive forces so that the molecules of water can break away from each other as gas molecules (steam).

The *heat of vaporization* of a substance is the number of calories required to convert one gram of liquid to one gram of gas without a change in temperature. A liquid has a different heat of vaporization at different temperatures. It is usually given, as in Table 7-4, at its normal boiling point unless otherwise stated. The reverse process, the changing of a gram of gas into a liquid without change in temperature, requires the removal of the same amount of heat energy (*heat of condensation*).

The heat needed to vaporize one mole of a substance is called the molar heat of vaporization or the *enthalpy of vaporization*,  $\Delta H_{vap}$ . The enthalpy of vaporization of water,  $\text{H}_2\text{O}$ , at its boiling point, as calculated from Table 7-4, is  $(18.015)(539.6)/1,000 = 9.721$  kcal/mole.

In Fig. 7-23 the result of adding heat energy to the element bro-

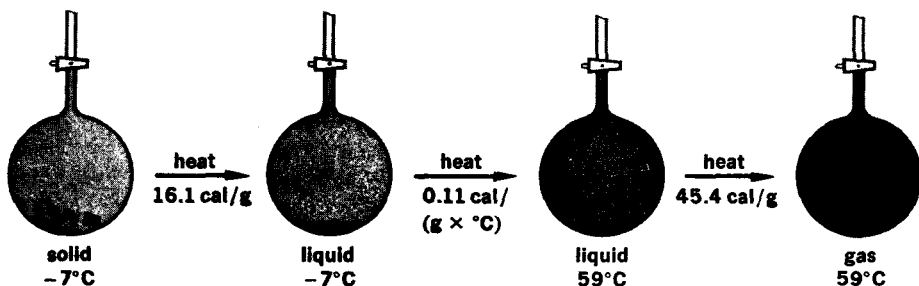


FIG. 7-23

Heat requirements to change solid bromine at its melting point to a gas at its boiling point. More complex apparatus than that shown here is needed to measure separately the processes of melting, heating, and vaporizing.

## STATES OF MATTER; KINETIC THEORY

mine is shown. As heat energy is progressively changed to kinetic energy, the van der Waals forces have less and less effect. Two abrupt changes in state are observed (1) when the solid bromine melts and (2) when the liquid bromine boils.

TABLE 7-4 *Heats of vaporization and fusion*

substance	heat of fusion, cal/g	heat of vaporization, cal/g
ammonia	108.1	327.1
benzene	30.3	94.3
carbon dioxide	45.3	87.2*
hydrogen chloride	14.0	98.7
mercury	2.8	67.8
oxygen	3.3	50.9
water	79.7	539.6

\* From solid carbon dioxide at  $-60^{\circ}\text{C}$ .

**PROBLEM 1** Calculate the amount of heat required to change 10 g of solid bromine at  $-7^{\circ}\text{C}$  to vapor at  $59^{\circ}\text{C}$ . (See Fig. 7-23 for data.)

*Solution*

$(16.1 \text{ cal/g})(10 \text{ g}) = 161 \text{ cal}$  to melt the bromine

$[0.107 \text{ cal}/(\text{g} \times \text{deg C})](10 \text{ g})(66^{\circ}) = 71 \text{ cal}$  to heat bromine from  $-7$  to  $59^{\circ}\text{C}$

$(45.4 \text{ cal/g})(10 \text{ g}) = 454 \text{ cal}$  to vaporize the bromine

total heat required =  $161 + 71 + 454 \text{ cal} = 686 \text{ cal}$

## CHAPTER REVIEW

### *Terms*

States of matter, solid, liquid, gaseous, compressibility, expansibility, diffusion, liquefaction, elastic collision, kinetic-molecular theory of gases, monatomic molecule, barometer, standard pressure, Boyle's law, Charles' law, absolute temperature, absolute zero, Kelvin scale, van der Waals forces, critical temperature, critical pressure, kinetic explanation of liquid state, vapor pressure, normal boiling point, kinetic explanation of solid state, vapor pressure of solids, sublimation, crystalline solid, X-ray diffraction by crystalline solids, ionic radii, determination of Avogadro's number, isometric, tetragonal, monoclinic, triclinic, orthorhombic, hexagonal, hexahedron, tetrahedron, octahedron, isomorphous, polymorphous, amorphous, melting point, specific heat, molar heat capacity, heat of fusion, enthalpy of fusion, heat of vaporization, enthalpy of vaporization.

### *Exercises*

1. A pound of liquid mercury at  $20^{\circ}\text{C}$  has a definite volume but an indefinite shape. Explain.

2. A pound of oxygen at  $20^{\circ}\text{C}$  may have any number of volumes, depending on what?
3. With respect to the atoms, molecules, or ions that compose a substance, what determines whether these particles are in the gaseous, liquid, or solid state at  $25^{\circ}\text{C}$ ?
4. Explain the following in terms of the kinetic theory of gases:
  - a. Drinking a liquid by means of a straw or glass tube.
  - b. A quantity of gas exerts twice the pressure when it is compressed to one-half of its original volume.
  - c. Hot air rises.
  - d. When a gas is cooled sufficiently, it liquefies.
  - e. When carbon dioxide is compressed sufficiently at  $20^{\circ}\text{C}$ , it liquefies; when oxygen at  $20^{\circ}\text{C}$  is compressed to an even greater extent, it does not liquefy.
  - f. A gas spreads more rapidly through a room when the temperature is  $35^{\circ}\text{C}$  than when the temperature is  $0^{\circ}\text{C}$ .
  - g. A gas released into quiet air at Denver, Colorado, diffuses more rapidly than when released into quiet air at the same temperature at Miami, Florida.
  - h. The air pressure in an automobile tire may rise considerably on driving some distance at a relatively high speed.
  - i. A bubble of air released at the bottom of a pool of water becomes larger as it approaches the surface.
5. Sulfur dioxide molecules ( $\text{SO}_2$ ) are twice as massive as oxygen molecules. Yet a collection of  $\text{O}_2$  molecules exerts the same pressure as a collection of  $\text{SO}_2$  molecules, provided that there are just as many  $\text{O}_2$  molecules as  $\text{SO}_2$  molecules and that each collection has the same volume and temperature. Explain in terms of the kinetic theory why the pressures are the same.
6. Consider an individual hydrogen molecule in a mixture of hydrogen and oxygen at  $25^{\circ}\text{C}$ . How might the velocity of this hydrogen molecule compare with the velocities of other hydrogen molecules in the mixture; with the velocities of oxygen molecules? If the hydrogen molecule under discussion were selected at random, would its kinetic energy most likely be approximately equal to, greater than, or less than the kinetic energy of an oxygen molecule, also selected at random.
7. Ten grams of argon has a volume of 5 liters at a certain temperature and pressure. How much smaller or larger is the pressure of 20 g of argon in a 2-liter container at the same temperature?
8. One limb of a manometer tube is connected to a glass bulb containing deuterium; the other limb is open to the atmosphere. The mercury level in the limb connected to the deuterium bulb stands 350 mm above the level in the other limb. In a nearby barometer the mercury level is 740 mm above the mercury reservoir. What is the pressure of the deuterium?
9. Explain how the mercury levels in the manometer described in Exercise 8 are changed if:
  - a. The temperature of deuterium is increased.



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THEORY**

- b. The whole apparatus and contents are transported at constant temperature to a higher altitude.
  - c. More deuterium is introduced into the bulb.
10. By means of the kinetic theory, explain how an ordinary thermometer gives a measure of the temperature of the medium in which it is immersed.
  11. If the pressure remains constant, how does the volume of a gas change as the temperature increases? Explain this behavior in theoretical terms.
  12. Convert the following temperatures to the absolute scale:  $30^{\circ}\text{C}$ ,  $-20^{\circ}\text{C}$ ,  $10^{\circ}\text{F}$ .
  13. The temperature of a volume of dry air is  $20^{\circ}\text{C}$ . What is the temperature of this air when it is heated at constant pressure to the point where its volume is twenty-five times the original volume; when it is cooled to the point where its volume is one-third of the original volume?
  14. Distinguish between boiling point and normal boiling point.
  15. Why does one feel cooler on emerging from a swimming pool into windy air than into still air at the same temperature?
  16. The atmospheric pressure on Mount *X* is 355 mm. What is the boiling point of water on Mount *X*? Would a pressure cooker be of any value on this mountain for the cooking of food? Explain.
  17. How does the formation of snow differ from that of hail or sleet? What special term is used to describe the former process?
  18. A small sample of powdered crystalline *X* is irradiated with an X-ray beam of 1.540 Å wavelength. Angle  $\theta$  for the most intense pair of lines was determined as  $22^{\circ}30'$ . Assuming this angle to be the diffraction for  $n = 1$ , calculate the distance between the ions in the two planes.
  19. Before X-rays could be used to determine the structure of a crystalline compound, their wavelength had to be determined experimentally, and, interestingly, the Bragg equation was developed for this purpose. W. H. and W. L. Bragg were able to calculate the distances between successive planes parallel to the faces of a sodium chloride crystal from the molar weight of NaCl, the Avogadro number, and the density of NaCl. Such calculations gave a value of about 2.82 Å between  $\text{Na}^{+}$  and  $\text{Cl}^{-}$  ions. Sodium chloride was then subjected to X-ray diffraction to determine the angle  $\theta$ , from which the X-ray wavelength was calculated. Suppose that an X-ray tube with a platinum anode was used as the source of the X-rays and that angle  $\theta$  for  $n = 1, 2$ , and 3 was found to be  $11^{\circ}36'$ ,  $23^{\circ}34'$ , and  $36^{\circ}40'$ , respectively. Calculate the X-ray wavelength emitted by platinum.
  20. On page 180 it was stated that the Avogadro number could be determined by X-ray measurements. In light of statements made in Exercise 20, would you surmise that other methods were available prior to the development of the X-ray method? Why?
  21. We may say that sodium nitrate and calcium carbonate are isomorphous but that only calcium carbonate is polymorphous. Explain.

22. We may describe sulfur variously as polymorphic, crystalline, or amorphous. Explain.
23. "A sample of liquid water is cooled to  $-10^{\circ}\text{C}$  without a change of state occurring. A small fragment of ice is then dropped into the liquid water, whereupon the water starts to freeze. Therefore, the freezing point of water is  $-10^{\circ}\text{C}$ ." If we assume that the first two sentences are true, may we also accept  $-10^{\circ}\text{C}$  as the freezing point of water? Explain.
24. What is the maximum height to which a liquid can be raised in a vertical pipe by means of a suction pump attached to the top of the pipe? Would the density of the liquid have a bearing on the height? Explain. Would the vapor pressure of the liquid have a bearing? Explain. Would the location of the liquid with respect to altitude have a bearing? Explain.
25. Calculate the temperature to which 10 g of gold at  $20^{\circ}\text{C}$  could be heated by the heat given off when 10 g of aluminum is cooled from 200 to  $180^{\circ}\text{C}$ .
26. Would the kinetic theory of gases indicate that the molar heat capacities of helium and neon are the same at  $20^{\circ}\text{C}$ ? Why? Would you expect their specific heats to be the same? Why?
27. Calculate the enthalpy of fusion,  $\Delta H_{fus}$ , of: benzene ( $\text{C}_6\text{H}_6$ ), water, mercury.
28. Calculate the enthalpy of vaporization,  $\Delta H_{vap}$ , of: hydrogen chloride, oxygen, water.
29. Calculate the amount of heat required to change 10 g of ice at  $-10^{\circ}\text{C}$  to steam at  $110^{\circ}\text{C}$ . (The specific heats of ice and steam are approximately the same.)
30. Heat energy is supplied uniformly at the rate of 100 cal/min to a 100-g sample of water, initially solid at  $-10^{\circ}\text{C}$ , till the water is converted into a gas at  $100^{\circ}\text{C}$ . How much time is required for the process to occur? Plot the change in temperature versus time.
31. What is the vapor pressure of ice at  $0^{\circ}\text{C}$ ; of water at  $0^{\circ}\text{C}$ ? Which evaporates more rapidly at  $0^{\circ}\text{C}$ , ice or water? Why?
32. In the text discussion of Fig. 7-6, it is stated that above  $100^{\circ}\text{C}$  the evaporation of mercury begins to add to the volume of trapped gas. How could the added volume due to mercury be experimentally determined at various temperatures?
33. Convert a tire pressure of 24 lb/sq in. to kg/sq cm. (The latter scale of pressures is used in European countries.)
34. To the right are listed values  $d$  value, A relative intensity  
for the four most intense X-ray 2.81 1.00  
powder diffraction lines for 1.99 0.83  
NaCl. Based on these and other 1.63 0.33  
measurements, the experimental 1.25 0.33  
values for the radii of the ions  
are  $\text{Na}^+$ , 0.98 Å, and  $\text{Cl}^-$ , 1.81 Å. By means of a diagram drawn to

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scale, show the planes in the NaCl crystal that correspond to the given  $d$  values. (The radius of  $\text{Na}^+$  in Table 19.1 of 0.95 Å is calculated on the basis of further considerations; 0.98 Å is the best experimental value.)

35. Using the radii of the ions given in Exercise 34 and the atomic weights, calculate the ideal density of sodium chloride in grams per cc.

## SUPPLEMENTARY READING

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# CALCULATIONS

## INVOLVING

### GAS LAWS



The chemist is often called on to handle and measure samples of gaseous substances. Because the densities of gases are so low, it is usually not convenient to determine the amount of gas in a container by measuring the weight of the gas. It is easier and generally more precise to measure the volume and then calculate the weight.

For a given mass<sup>1</sup> of gas the important variables are the pressure, the volume, and the temperature:  $P$ ,  $V$ , and  $T$ ; if gas is added or taken away, the mass  $m$  also varies. Because all gases behave in a similar fashion, we speak of the general rules of behavior as the gas laws. We have taken up two of these laws qualitatively, Boyle's law and Charles' law. In the following sections we shall show how these and several other laws are applied in a quantitative way in the solution of problems.

#### BOYLE'S LAW

*The volume of a certain mass of gas is inversely proportional to the pressure, at constant temperature.* This is Boyle's law, discovered by Robert Boyle in 1660. Stated mathematically:

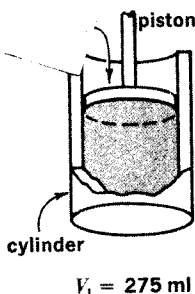
$$\frac{V_1}{V_2} = \frac{P_2}{P_1}$$

or

$$P_1 V_1 = P_2 V_2$$

The symbols  $V_1$  and  $P_1$  refer to the original volume and pressure,

<sup>1</sup> The term "certain mass of gas" or "given mass of gas" is used to show that the amount of matter does not change during the experiments. The pressure, or the volume, or the temperature may change, but the number of molecules being studied does not.



$V_2$  and  $P_2$  to the volume and pressure under the new or changed conditions.

**PROBLEM 1** A sample of gas weighing 0.216 g is trapped in a cylinder by a piston, as shown in Fig. 8-1. The volume of the gas is 275 ml when the pressure exerted by the piston is equal to 920 mm. If the pressure is decreased to 780 mm, what is the volume?

To hold a given quantity of gas in this cylinder at a volume of 275 ml, a pressure of 920 mm must be maintained by the piston. If this pressure is reduced, the gas will force the piston outward and occupy a larger volume.

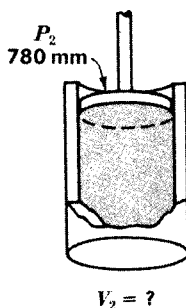


FIG. 8-1

**Analysis** In working gas-law problems, we are usually interested in four variable quantities: the amount (expressed in mass or in number of molecules), the pressure, the volume, and the temperature. It helps in analyzing a problem to tabulate the data available for the original condition of the gas and for its new or changed condition. If one of the four variables does not change, this is indicated by the symbol  $k$  (standing for *constant*). The language of Problem 1 implies that the cylinder does not leak, so that we assume that the mass of gas remains constant at 0.216 g. Because the temperature is not mentioned, we must assume that its initial and final values are the same<sup>1</sup>. We arrange our data as follows:

	$m$	$P$	$V$	$T$
original	$k$	920 mm	275 ml	$k$
changed to	$k$	780 mm	$V_2$	$k$

We might reason as follows. Only the volume and the pressure change, so that Boyle's law applies. The pressure is decreased, and therefore the volume must be increased. The changed volume is greater than 275 ml.

For gas-law problems in this text, we shall find that all calculations involve either a direct or an indirect *proportion*. Such calculations can be made in a straightforward manner by using ratios or factors based on the variables that change in value. In Problem 1,

$$V_2 = 275 \text{ ml} \times \frac{\text{pressure}}{\text{pressure}}$$

$\underbrace{\quad}_{\text{new volume}} \quad \underbrace{\quad}_{\text{original volume}} \quad \underbrace{\quad}_{\text{factor to account for pressure change}}$

<sup>1</sup> A word about gas laws in general. The idea of holding one experimental condition *constant* may not be easily understood at first. For instance, consider the application of Boyle's law to a case in which the pressure is increased and we are asked to calculate the change in volume. Most persons know that, if the pressure on a gas is suddenly increased, the gas becomes hotter. This thought is troublesome; how can we calculate the new volume of the gas as though the temperature did not change, when the mere application of pressure causes the temperature to change?

In applying Boyle's law to this type of change, we may think of the pressure being exerted so slowly that the heat generated escapes without changing the temperature; or we may think of exerting the pressure all at once, allowing the temperature to rise, and then cooling the gas back to the original temperature. The important thing in using Boyle's law is that the original and final temperatures are the same.

For gas-law applications in general, a *constant* condition (for example, temperature, pressure, or volume) is provided for in a problem or experiment by having the original and the final condition the same.

We know that the volume depends on the pressure, so that our only problem here is to decide which factor to use:  $\frac{920 \text{ mm}}{780 \text{ mm}}$  or  $\frac{780 \text{ mm}}{920 \text{ mm}}$ . The first of these factors has a value greater than 1; the second has a value less than 1. Because we reasoned that the volume of the gas will be greater than 275 ml, we choose the factor  $\frac{920 \text{ mm}}{780 \text{ mm}}$ . We know that, if we use it as a multiplier, the numerical answer will be greater than 275 ml.

*Solution*

$$V_2 = 275 \text{ ml} \times \frac{920 \text{ mm}}{780 \text{ mm}}$$

└ factor to correct for pressure change

$$= 324 \text{ ml}$$

*Check* We can do much toward improving our efficiency in solving problems by inspecting the answer to see if it is reasonable. Because the answer to a problem usually includes two parts—the units and the number—this inspection should cover both phases. In this problem we note that units have canceled to leave units of volume (milliliters); thus we find that this part is correct. In checking the size of the answer, we note that the new volume is greater than 275 ml, as we predicted it would be. Because the correction factor,  $\frac{920 \text{ mm}}{780 \text{ mm}}$ , is about 6/5 (divide each member by 15), the new volume should be only about 1/5 larger because of the pressure decrease, that is, about  $275 \text{ ml} + 1/5 \text{ of } 275 \text{ ml}$ , or about 330 ml. Therefore the answer 324 ml seems reasonable.

## CHARLES' LAW

*The volume of a given mass of gas is directly proportional to the absolute temperature, at constant pressure.* This is Charles' law, discovered by Jacques Charles in 1787. Stated mathematically:

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}$$

**PROBLEM 2** A child's balloon has a volume of 3.80 liters (about a gallon) when the temperature is 35°C. What is the volume if the balloon is put into a refrigerator and cooled to 5°C? Assume that the pressure inside the balloon is equal to the atmospheric pressure at all times.

*Analysis* Tabulate the data. Because we can use only absolute temperatures in gas-law calculations, other scales of temperature must be converted to the absolute scale:  $^{\circ}\text{C} + 273^{\circ} = ^{\circ}\text{K}$ .

	<i>m</i>	<i>V</i>	<i>T</i>	<i>P</i>
original	<i>k</i>	3.80 liters	308°K	<i>k</i>
changed to	<i>k</i>	<i>V</i> <sub>2</sub>	278°K	<i>k</i>

We can calculate the new volume by multiplying the old volume by a factor that expresses the influence of temperature on volume.

$$V_2 = 3.80 \text{ liters} \times \frac{\text{temperature}}{\text{temperature}}$$

$\underbrace{\hspace{1.5cm}}_{\text{new volume}} \quad \underbrace{\hspace{1.5cm}}_{\text{original volume}} \quad \underbrace{\hspace{2.5cm}}_{\text{factor to account for temperature change}}$

Charles' law is the guide in choosing the proper temperature factor. According to this law, when the temperature decreases, the volume must decrease proportionately. We use the temperature factor  $\frac{278^\circ\text{K}}{308^\circ\text{K}}$ , because it is less than 1.

*Solution*

$$V_2 = 3.80 \text{ liters} \times \frac{278^\circ\text{K}}{308^\circ\text{K}}$$

$\underbrace{\hspace{2.5cm}}_{\text{factor to correct for temperature change}}$

$$= 3.43 \text{ liters}$$

*Check* We note that units cancel to give units of volume. Further, the calculated volume is smaller, as was predicted. The factor  $\frac{278^\circ\text{K}}{308^\circ\text{K}}$  is equal to about 9/10, so that we expect the new volume to be about 9/10 of 3.80 liters, or about 3.4 liters.

## RELATION OF PRESSURE AND TEMPERATURE

*The pressure of a given mass of gas is directly proportional to the absolute temperature if the volume does not change.*<sup>1</sup> Stated mathematically:

$$\frac{P_1}{P_2} = \frac{T_1}{T_2}$$

**PROBLEM 3** A steel cylinder of oxygen gas has a pressure of 135 atm at a temperature of 20°C (Fig. 8-2). Suppose that the cylinder becomes heated to 85° because it is stored near a steam radiator. Calculate the pressure inside the cylinder at the higher temperature.

A steel cylinder of oxygen gas with a gauge for measuring the pressure.

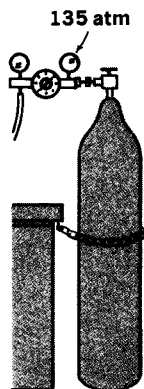


FIG. 8-2

*Analysis* The gas is stored in a steel cylinder, so that we can assume that its mass does not change at all and that the volume does not change appreciably. The two variables are the pressure and temperature.

	<i>m</i>	<i>V</i>	<i>P</i>	<i>T</i>
original	<i>k</i>	<i>k</i>	135 atm	293°K
changed to	<i>k</i>	<i>k</i>	<i>P</i> <sub>2</sub>	358°K

It is logical to reason as follows. The temperature is increasing; the mole-

<sup>1</sup> This is sometimes called Gay-Lussac's law, sometimes Amontons' law, after Guillaume Amontons who related the pressure of a gas to its temperature and constructed a gas thermometer on this basis in 1703.

cules move about in the cylinder more rapidly, hitting one another and the walls of the cylinder more often and with greater force. Therefore the pressure increases. We use the temperature factor  $\frac{358^{\circ}\text{K}}{293^{\circ}\text{K}}$ .

*Solution*

$$P_2 = 135 \text{ atm} \times \frac{358^{\circ}\text{K}}{293^{\circ}\text{K}}$$

└ factor to account for  
temperature change

$$= 165 \text{ atm}$$

*Check* We expect the pressure to be larger by about 1/5, that is, by about 30 atm, because the factor  $\frac{358^{\circ}}{293^{\circ}}$  is about 1/5 larger than 1:  $\frac{358}{293} = \frac{293+65}{293}$ , and  $\frac{65}{293} \approx \frac{1}{5}$ . The calculated answer agrees with the predicted answer in both magnitude and units.

## DALTON'S LAW OF PARTIAL PRESSURES

In a mixture of different gases each gas exerts part of the pressure. This is the same pressure that it would exert if it alone occupied the volume containing the mixed gases. *The total pressure in a mixture of gases is the sum of the individual partial pressures.* This is Dalton's law, formulated by John Dalton about 1803. Stated mathematically:

$$P = p_1 + p_2 + p_3 + \dots$$

$P$  is the total pressure; the small  $p$ 's refer to the part of the pressure exerted by each different gaseous substance in the mixture.

When a sample of gas, air for example, is measured over water, the pressure of the gas equals the atmospheric pressure, provided the water inside the graduated cylinder is at the same level as it is outside. Note in the detailed drawing that the gas contains water molecules as well as air molecules. Part of the gas pressure is due to water molecules.

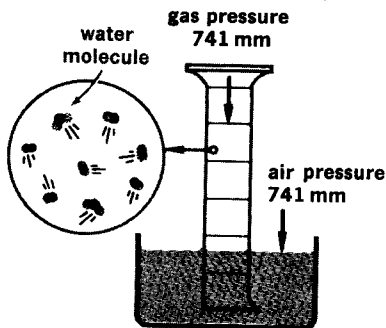


FIG. 8-3

**PROBLEM 4** A sample of air held in a graduated cylinder over water has a volume of 88.3 ml at a temperature of  $18.5^{\circ}\text{C}$  and a pressure of 741 mm (Fig. 8-3). What would the volume of the air be if it were dry and at the same temperature and pressure?

*Analysis* The air trapped in the cylinder is saturated with water vapor; the total pressure of 741 mm is the sum of the pressures of the air plus the



# CALCULATIONS INVOLVING GAS LAWS

water vapor. At 18.5°C the vapor pressure of water is approximately 16 mm (see Table 2 in the Appendix).

$$P_{\text{total}} = p_{\text{dry air}} + p_{\text{water vapor}} \quad (\text{Dalton's law})$$

or

$$\begin{aligned} p_{\text{dry air}} &= P_{\text{total}} - p_{\text{water vapor}} \\ &= 741 \text{ mm} - 16 \text{ mm} \\ &= 725 \text{ mm} \end{aligned}$$

Collecting our data, we have

	<i>m</i>	<i>V</i>	<i>P</i>	<i>T</i>
Original	<i>k</i>	88.3 ml	725 mm	<i>k</i>
changed to	<i>k</i>	<i>V</i> <sub>2</sub>	741 mm	<i>k</i>

Note that in the "changed" condition the dry air exerts the entire pressure of 741 mm. Consequently, the volume of the dry air must be smaller. The correction factor is  $\frac{725 \text{ mm}}{741 \text{ mm}}$ .

*Solution*

$$\begin{aligned} V_2 &= 88.3 \text{ ml} \times \frac{725 \text{ mm}}{741 \text{ mm}} \\ &\quad \left[ \begin{array}{l} \text{pressure factor must} \\ \text{account for decrease,} \\ \text{therefore the smaller} \\ \text{value is over the larger} \end{array} \right] \\ &= 86.4 \text{ ml} \end{aligned}$$

*Check* The fraction  $\frac{725}{741}$  is only slightly smaller than 1. The new volume is slightly less than 88.3 ml.

**PROBLEM 5** A sample of hydrogen is collected in a bottle over water. By carefully raising and lowering the bottle, the height of the water inside is adjusted so that it is just even with the water level outside (see Fig. 8-4).

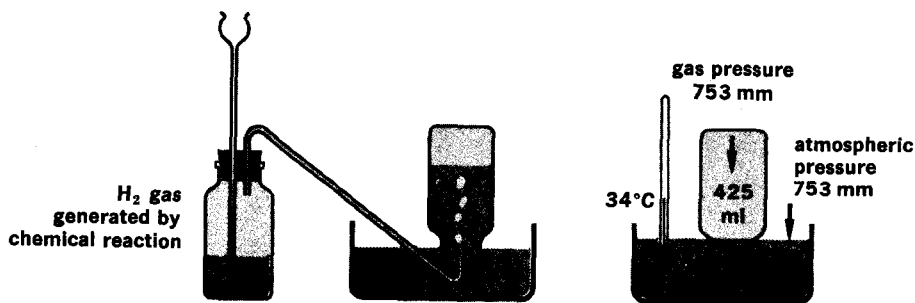


FIG. 8-4

When a sample of gas is collected, its pressure, its volume, and its temperature are measured. It is often convenient to measure the latter two when the gas is held at the pressure of the atmosphere. The pressure of the atmosphere is read on a nearby barometer.

The following measurements are taken: volume of gas, 425 ml; atmospheric pressure, 753 mm; temperature of water (and of gas also), 34°C. Calculate the volume the hydrogen would have if it were dry and at a pressure of 760 mm and a temperature of 0°C.

*Analysis* The hydrogen is mixed with water vapor, therefore not all of the 753 mm pressure is due to hydrogen; a small part is due to the water vapor. The vapor pressure of water varies with the temperature, so we find from Table 2 in the Appendix that its value at 34°C is 40 mm. The pressure due to hydrogen can now be calculated by means of Dalton's law.

$$P_{\text{total}} = p_{\text{H}_2} + p_{\text{H}_2\text{O}}$$

or

$$p_{\text{H}_2} = P_{\text{total}} - p_{\text{H}_2\text{O}}$$

$$= 753 \text{ mm} - 40 \text{ mm} = 713 \text{ mm}$$

That is, if the water vapor<sup>1</sup> is removed so that hydrogen alone occupies the entire volume, the pressure will fall from 753 mm to 713 mm. This latter pressure is the one that we must use as the original pressure in solving for the volume of the dry hydrogen at 0°C and 760 mm:

	<i>m</i>	<i>V</i>	<i>T</i>	<i>P</i>
original	<i>k</i>	425 ml	307°K	713 mm
changed to	<i>k</i>	<i>V</i> <sub>2</sub>	273°K	760 mm

$$V_2 = 425 \text{ ml} \times \frac{\text{temperature}}{\text{temperature}} \times \frac{\text{pressure}}{\text{pressure}}$$

$\downarrow$  new volume                       $\downarrow$  to correct for temperature change                       $\downarrow$  to correct for pressure change

The pressure of 760 mm is greater than the pressure exerted by hydrogen when it was collected over water. The volume of the hydrogen tends to be less because of this change in pressure. The pressure factor is set at  $\frac{713 \text{ mm}}{760 \text{ mm}}$  (Boyle's law).

The temperature of 0°C is lower than 34°C; there tends to be a decrease in volume because of this decrease in temperature. The temperature factor is set as  $\frac{273^\circ\text{K}}{307^\circ\text{K}}$  (Charles' law).

*Solution*

$$V_2 = 425 \text{ ml} \times \frac{273^\circ\text{K}}{307^\circ\text{K}} \times \frac{713 \text{ mm}}{760 \text{ mm}}$$

$\downarrow$  factor to correct for temperature change                       $\downarrow$  factor to correct for pressure change

$$V_2 = 355 \text{ ml}$$

*Check* The method of checking an answer for obvious errors has been described in earlier problems. The job of inspecting answers to problems is left to the student's ingenuity and initiative for the remainder of this chapter.

<sup>1</sup> The wet gas could be passed through a drying agent such as calcium chloride.

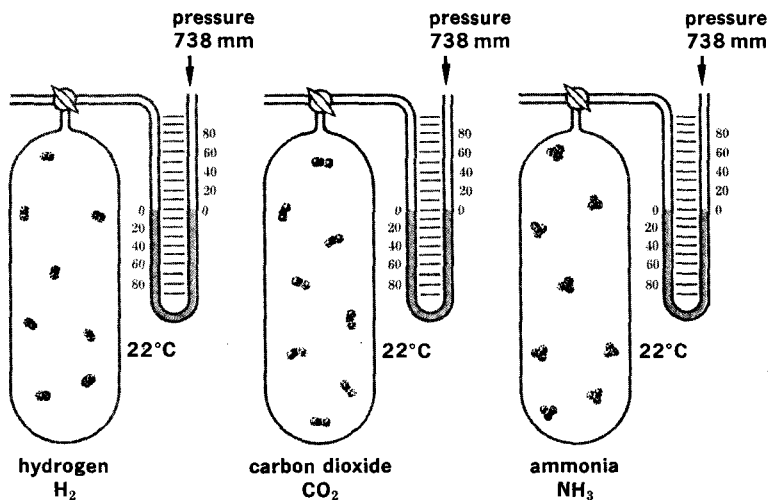


FIG. 8-5

A schematic representation of Avogadro's law.

### AVOGADRO'S LAW

At a set pressure and temperature a vessel of a given volume contains a certain number of molecules of gas. The kind of gas does not matter. *Equal numbers of molecules are contained in equal volumes of different gases if the pressure and temperature are the same.* This is Avogadro's law, formulated by Amadeo Avogadro in 1811.

For example, the number of molecules of nitrogen in 1 liter at a pressure of 900 mm and a temperature of 25°C is definite. At the same volume, pressure, and temperature there could be present, instead, the same number of hydrogen molecules or carbon dioxide molecules or molecules of any other gas (Fig. 8-5). If the pressure were higher, more molecules would be crowded into the same volume. If, however, the temperature were higher, there would not be room for so many molecules in the same volume at the same pressure.

Because the pressure and temperature directly affect the amount of gas present in any measured volume, it is necessary to specify all three variables,  $P$ ,  $V$ , and  $T$ , when speaking of a certain amount of gas. Often only the volume of a gas is specified, for example, 3.5 liters of nitrogen. In such a case it is taken for granted that the pressure of the gas is 760 mm and the temperature is 0°C. These values are the **standard conditions** of pressure and temperature used for the measurement of gases the world over. The volume of a gas at these standard conditions is commonly stated to be the **volume at STP** (standard temperature and pressure).

**PROBLEM 6** Compare the number of H<sub>2</sub> and N<sub>2</sub> molecules in two containers described as follows: A 2-liter container of hydrogen filled at 127°C and 5 atm; a 5-liter container of nitrogen filled at 27°C and 3 atm.

*Analysis* The data are tabulated as follows:

	<i>V</i>	<i>T</i>	<i>P</i>
hydrogen	2 liters	400°K	5 atm
nitrogen	5 liters	300°K	3 atm

We can multiply the number of H<sub>2</sub> molecules by factors to see how many times larger or smaller the number of N<sub>2</sub> molecules is. The volume factor is set  $\frac{5 \text{ liters}}{2 \text{ liters}}$ , because a larger volume contains a larger number of molecules.

Because a container filled at a lower temperature contains a larger number of molecules, the temperature factor is set  $\frac{400^\circ\text{K}}{300^\circ\text{K}}$ . A container filled at a lower pressure contains fewer molecules, so that the pressure factor is set  $\frac{3 \text{ atm}}{5 \text{ atm}}$ .

*Solution*

$$\begin{aligned} \text{no. of N}_2 &= \text{no. of H}_2 \times \frac{5 \text{ liters}}{2 \text{ liters}} \times \frac{400^\circ\text{K}}{300^\circ\text{K}} \times \frac{3 \text{ atm}}{5 \text{ atm}} \\ &= 2(\text{no. of H}_2); \text{ that is, there are twice as many N}_2 \\ &\quad \text{molecules as H}_2 \text{ molecules} \end{aligned}$$

## GRAHAM'S LAW OF DIFFUSION

A gas that has a high density diffuses more slowly than one with a lower density. *The rates of diffusion of two gases are inversely proportional to the square roots of their densities.* This is Graham's law, discovered by Thomas Graham in 1881. Stated mathematically:

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}}$$

**PROBLEM 7** At standard conditions 1 liter of oxygen gas weighs almost 1.44 g, whereas 1 liter of hydrogen weighs only 0.09 g. Which gas diffuses faster? Calculate how much faster.

*Analysis*

rates	densities, g/liter
$r_{\text{H}_2}$	$d_{\text{H}_2} = 0.09$
$r_{\text{O}_2}$	$d_{\text{O}_2} = 1.44$

The rates of diffusion are related to the square roots of the densities, so that we can solve this problem by using Graham's law. According to the law, a logical statement would be: The hydrogen will diffuse faster, because it has the lower density.

The factor is  $\frac{\sqrt{1.44 \text{ g/liter}}}{\sqrt{0.09 \text{ g/liter}}}$ .

*Solution*

$$r_{\text{H}_2} = r_{\text{O}_2} \times \frac{\sqrt{1.44}}{\sqrt{0.09}}$$

The equation is arranged in a logical way. We have decided that  $r_{\text{H}_2}$  is greater than  $r_{\text{O}_2}$ , so we know that the multiplier for  $r_{\text{O}_2}$  must be greater than 1 if the equation is to be correct:

$$r_{\text{H}_2} = r_{\text{O}_2} \times \frac{1.2}{0.3} = 4r_{\text{O}_2}$$

*Check* Our solution to the problem is that the diffusion rate of hydrogen is four times that of oxygen. This checks with the prediction made in the analysis.

## EXPERIMENTAL MOLECULAR WEIGHTS

Through the nineteenth century precise methods were not available for counting atoms or molecules, that is, for determining Avogadro's number. Hence, the *absolute weight* of a single atom or molecule was unknown. However, several methods were developed for comparing the *relative weights* of molecules of different substances with one another. To make these comparisons, oxygen was chosen as the reference substance, and the relative weight of an oxygen atom was arbitrarily assigned a value of 16 awu; the  $\text{O}_2$  molecule then had a relative weight of 32 awu.<sup>1</sup>

Two of the early methods for determining the relative weights of molecules depend on certain properties of gases that have been discussed in this chapter. One method is based on differences in gas densities and the other on the differences in rates of diffusion or effusion.

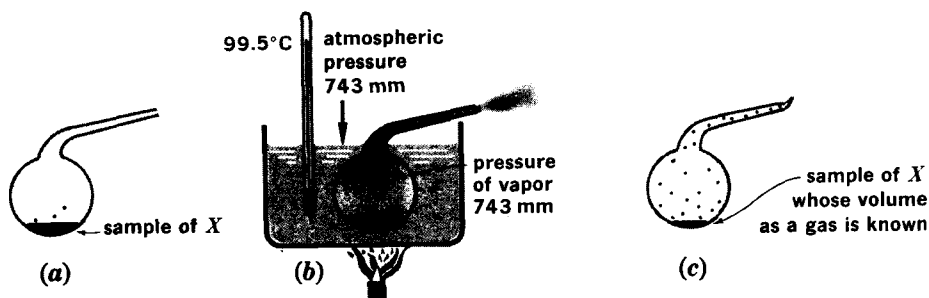
*Relative Weights from Gas Densities.* To determine the molecular weight of a substance, we can compare the gas density of the pure substance with the gas density of oxygen, both densities being measured at the same temperature and pressure. For example, 1 liter of methane at  $0^\circ\text{C}$  and 760 mm weighs 0.7168 g; 1 liter of oxygen under the same conditions weighs twice as much, 1.4236 g. According to Avogadro's law, the same number of molecules are present in each liter, because they have the same temperature and pressure. Each methane molecule must be  $0.7168/1.4236 = 0.504$  times as heavy as an oxygen molecule. To account for the fact that a number of methane molecules weighs only half as much as the same number of oxygen molecules, we conclude that each methane molecule has a relative weight of (0.504) (32 awu) or 16.1 awu.

It is important to reemphasize that such comparisons and calculations were carried out before the actual number of molecules in a liter of gas could be determined.

<sup>1</sup> The fact that the choice of reference substance was changed from oxygen to carbon-12 in 1962 does not invalidate the methods used or the work done prior to 1962. The new standard does necessitate slight changes in atomic and molecular weights that were based on the old scale. The weight of an average  $\text{O}_2$  molecule on the new scale is 31.998 awu, and all other relative atomic and molecular weights are changed a proportionate amount.

Calculations of molecular weight from gas densities are simplified by focusing attention on *mole quantities*. The method can be outlined as follows:

1. The volume of 32 g of oxygen, 1 mole, has been experimentally determined as 22.4 liters at STP.
2. Based on Avogadro's law, 22.4 liters of any gas at STP constitutes 1 mole of that gas; 22.4 liters at STP is called the **molar gas volume**, or the volume of one mole.
3. The weight in grams of 22.4 liters at STP of a gas is the weight of 1 mole of that gas. This weight in grams is numerically equal to the relative weight of one molecule in atomic weight units. In the case of methane, the weight of 1 mole would be (0.7168 g/liter) (22.4 liters) = 16.1 g. The relative molecular weight is 16.1 awu.
4. The experimental determination of a relative molecular weight involves the careful measurement of the weight and volume of a sample of the gaseous substance at a known temperature and pressure (see Fig. 8-6). Knowing these four quantities we can use the appropriate gas laws to calculate the weight of 22.4 liters of the gaseous substance at 0°C and 760 mm (STP). Problem 8 illustrates a typical calculation.



**FIG. 8-6**

Molecular weight determination by the Dumas method. (a) Flask of known weight and volume contains sample (excess) of low-boiling liquid, *X*, whose molecular weight is to be determined. (b) The flask and sample are heated so that *X* is completely vaporized; all air is driven from the flask, and the tip of the flask is sealed with a flame. (c) The sealed flask, cooled to room temperature, is weighed to determine the weight of *X* trapped. From the weight and volume of gaseous *X* at 99.5°C and 743 mm, we can calculate the weight of 22.4 liters of gaseous *X* at STP.

**PROBLEM 8** A 1.40-liter volume of a gas measured at a temperature of 27°C and a pressure of 900 mm was found to weigh 2.273 g. Calculate the molecular weight of this gas.

**Analysis** We wish to calculate the weight in atomic weight units of one molecule of this gas. Because the molecular weight in atomic weight units is equal numerically to the weight of 1 mole in grams, we calculate the weight of 1 mole of the gas. The weight in grams of this quantity of gas will reveal the molecular weight.

# CALCULATIONS INVOLVING GAS LAWS

One mole of gas occupies 22.4 liters at 0°C and 760 mm, so that the data are tabulated as follows:

	$m$	$V$	$T$	$P$
original	2.273 g	1.40 liters	300°K	900 mm
changed to	$m_2$	22.4 liters	273°K	760 mm
(as calculated)	└ mass of 1 mole of this gas		└ conditions that define 1 mole of a gas	

Using these data, we wish to formulate an equation that can be solved to give the weight of 1 mole,  $m_2$ :

$$m_2 = 2.273 \text{ g} \times \frac{\text{volume}}{\text{volume}} \times \frac{\text{temperature}}{\text{temperature}} \times \frac{\text{pressure}}{\text{pressure}}$$

The analysis is undertaken as before. We consider separately how each of the three changes in conditions affects the mass of the gas.

Change in volume: There is an increase in volume; the weight of gas in 22.4 liters is much greater than the weight in 1.40 liters. The volume factor is  $\frac{22.4 \text{ liters}}{1.40 \text{ liters}}$ .

Change in temperature: There is a decrease in temperature. Because molecules move more slowly and tend to be closer together at lower temperatures, a container filled at 273°K holds more molecules or a greater mass of gas than when filled at 300°K. The temperature factor is  $\frac{300^\circ\text{K}}{273^\circ\text{K}}$ .

Change in pressure: There is a decrease in pressure; the mass of gas needed to exert 760 mm pressure is less than that needed to exert 900 mm pressure. The pressure factor is  $\frac{760 \text{ mm}}{900 \text{ mm}}$ .

*Solution* We set up an equation using the factors worked out in our analysis, cancel units, and solve:

$$\begin{aligned} m_2 &= 2.273 \text{ g} \times \frac{22.4 \text{ liters}}{1.40 \text{ liters}} \times \frac{300^\circ\text{K}}{273^\circ\text{K}} \times \frac{760 \text{ mm}}{900 \text{ mm}} \\ &= 33.7 \text{ g in 1 mole} \end{aligned}$$

The weight of 1 mole ( $6.02 \times 10^{23}$  molecules) in grams is equal numerically to the weight of one molecule in atomic weight units. Therefore, the weight of one molecule is 33.7 awu.

*Check* In estimating the answer, we note that the factor for the change in pressure just about offsets the factor for the change in temperature. The former tends to decrease the mass, the latter to increase the mass. The change in volume has a large effect, causing the mass to increase about fifteen-fold. Rounding off the first mass to 2.3 g and multiplying by 15, we obtain an estimated answer of 34 or 35 g for the weight of 1 mole. The estimated weight of a molecule is therefore 34 or 35 awu. The calculated answer agrees in both units and magnitude with this estimation.

*Relative Weights from Rates of Effusion.* According to Avogadro's law, the densities of gases are proportional to their molecular weights.

We may therefore substitute *molecular weight* for *density* in the expression of Graham's law of diffusion:

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{\text{mol. wt}_2}}{\sqrt{\text{mol. wt}_1}}$$

This relationship also expresses the rate of *effusion* of a gas through a small hole into an evacuated region. That is, if a tiny hole is made in a thin wall of a container filled with a gas, gas molecules pass through the hole into an evacuated space at a rate inversely proportional to the square root of the weight of the molecules.

In order to determine molecular weights by this method, the time required for a given volume of the gas to effuse through a small hole is compared with the time required for the same volume of oxygen to effuse through the same hole. Effusion times can be measured with an apparatus similar to that shown in Fig. 8-7. Very little error is introduced by allowing the gases to effuse into air rather than an evacuated chamber, provided the molecular weights of the two gases to be compared are not greatly different. The following problem serves to show what measurements are made and how the molecular weight is calculated.

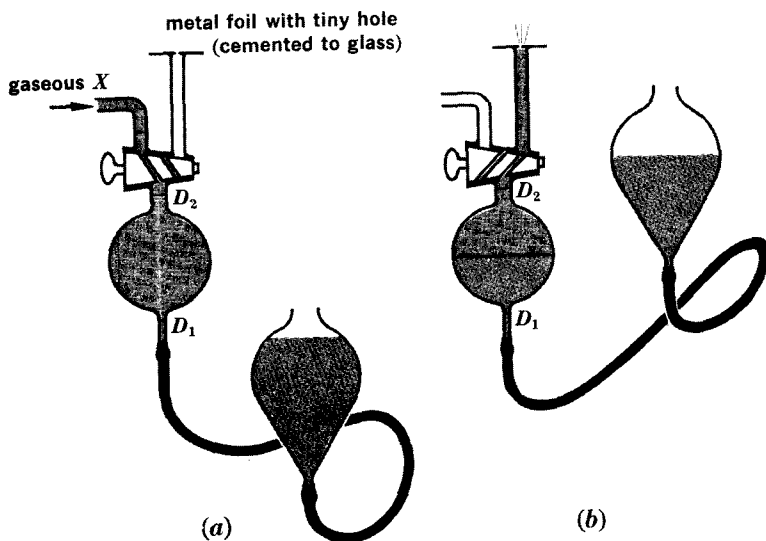


FIG. 8-7

Molecular weight determined by effusion method. (a) The mercury bulb is lowered to allow the sample bulb to fill with gaseous  $X$ . (b) After filling, the two-way stopcock is closed and the mercury bulb elevated. With the apparatus completely filled with  $X$ , the stopcock is opened to the right limb, and the time necessary for the mercury to flow from  $D_1$  to  $D_2$  is noted. The effusion time required for an equal volume of gas of known molecular weight is determined in a similar manner.



## CALCULATIONS INVOLVING GAS LAWS

**PROBLEM 9** The time required for a volume of gas X to effuse through a small hole was 112.2 sec. The time required for the same volume of oxygen was 84.7 sec. Calculate the molecular weight of gas X.

*Analysis* Since the time required for effusion is inversely proportional to the rate of effusion (the longer the time, the less the rate), we may further modify the Graham's law equation as follows:

$$\frac{r_1}{r_2} = \frac{t_2}{t_1} = \frac{\sqrt{\text{mol. wt}_2}}{\sqrt{\text{mol. wt}_1}}$$

or

$$\frac{t_{O_2}}{t_X} = \frac{\sqrt{32.0 \text{ awu}}}{\sqrt{\text{mol. wt of X}}}$$

*Solution*

$$\begin{aligned} \frac{84.7 \text{ sec}}{112.2 \text{ sec}} &= \frac{\sqrt{32.0 \text{ awu}}}{\sqrt{\text{mol. wt of X}}} \\ \text{mol. wt of X} &= \frac{112.2^2 \times 32.0 \text{ awu}}{84.7^2} \\ &= 56.2 \text{ awu} \end{aligned}$$

It is interesting to note that the molecular weight (or atomic weight) of the noble gas radon was determined by the effusion method in 1910, two years after its isolation.

**MEAN FREE PATH.** The average distance that a gaseous molecule travels before colliding with another molecule is called its *mean free path*. In gases such as oxygen, nitrogen, and air at STP the distance that a molecule travels before colliding with another molecule is about 500 to 700 Å. (These molecules have diameters of about 2 Å.) In an effusion experiment, the diameter and the length of the hole are made very small, so that a molecule moving through the hole has as few collisions as possible. When the hole is large or the wall thick, many collisions occur in the hole. The gas then flows or streams through the hole instead of effusing through.

In an ideal gas, the mean free path of a gas molecule is determined only by its diameter and concentration.

## REPRESENTATIVE GAS LAW PROBLEMS

In the following problems, we simply state the problem and then indicate the solution without giving an analysis. It will be good practice for you to analyze each solution, to satisfy yourself that the factors are set up correctly, and to calculate the answers, canceling units as needed.

**PROBLEM 10** The molecular weight of ozone,  $O_3$ , is 48 awu. Calculate the density of ozone in grams per liter at  $20^\circ\text{C}$  and 740 mm.

	$m$	$V$	$T$	$P$
known	48 g	22.4 liters	$273^\circ\text{K}$	760 mm
changed to	$m_2$	1 liter	$293^\circ\text{K}$	740 mm

$$m_2 = 48 \text{ g} \times \frac{1 \text{ liter}}{22.4 \text{ liters}} \times \frac{273^\circ\text{K}}{293^\circ\text{K}} \times \frac{740 \text{ mm}}{760 \text{ mm}}$$

(Note:  $m_2$  is the weight in grams of 1 liter at  $20^\circ\text{C}$  and 740 mm.)

**PROBLEM 11** Calculate the pressure in pounds per square inch exerted by 100 g of nitrogen,  $\text{N}_2$ , when confined at  $-10^\circ\text{C}$  in a cylinder whose volume is 3.10 gal.

	$m$	$V$	$T$	$P$
known	28 g	5.94 gal (22.4 liters)	$273^\circ\text{K}$	14.7 psi (760 mm)
changed to	100 g	3.10 gal	$263^\circ\text{K}$	$P_2$

$$P_2 = 14.7 \text{ psi} \times \frac{100 \text{ g}}{28 \text{ g}} \times \frac{5.94 \text{ gal}}{3.10 \text{ gal}} \times \frac{263^\circ\text{K}}{273^\circ\text{K}}$$

**PROBLEM 12** A cylinder contains oxygen,  $\text{O}_2$ , at a pressure of 10 atm and a temperature of  $27^\circ\text{C}$ . The volume of the cylinder is 10 liters. What is the weight of the oxygen?

	$m$	$V$	$T$	$P$
known	32 g	22.4 liters	$273^\circ\text{K}$	1 atm
changed to	$m_2$	10 liters	$300^\circ\text{K}$	10 atm

$$m_2 = 32 \text{ g} \times \frac{10 \text{ liters}}{22.4 \text{ liters}} \times \frac{273^\circ\text{K}}{300^\circ\text{K}} \times \frac{10 \text{ atm}}{1 \text{ atm}}$$

**PROBLEM 13** A 1-liter container (1.00 liter) filled with hydrogen,  $\text{H}_2$ , at  $20^\circ$  and 740 mm is evacuated with a vacuum pump until the pressure gauge reads  $1 \times 10^{-4}$  mm (a rather poor vacuum). Calculate the number of hydrogen molecules remaining in the container.

	$n$	$V$	$T$	$P$
known	$6.02 \times 10^{23}$ molecules	22.4 liters	$273^\circ\text{K}$	760 mm
changed to	$x_2$	1.00 liter	$293^\circ\text{K}$	$1 \times 10^{-4}$ mm

$$x_2 = 6.02 \times 10^{23} \text{ molecules} \times \frac{1.00 \text{ liter}}{22.4 \text{ liters}} \times \frac{273^\circ\text{K}}{293^\circ\text{K}} \times \frac{1 \times 10^{-4} \text{ mm}}{760 \text{ mm}}$$

**PROBLEM 14** Refer to Problem 13; there is still a large number of hydrogen molecules in the container. Suppose that we wish to remove all the hydrogen molecules but that it will not matter (for the use to which the container is to be put) if a small amount of some other gas—helium, for example—is present. In order to remove the residual hydrogen (after pumping down to  $1 \times 10^{-4}$  mm), the container is filled with helium to a pressure of 760 mm and then evacuated to a pressure of  $1 \times 10^{-4}$  mm. Each time this is done, a large fraction of the hydrogen is flushed out with the helium. If this filling with helium and then pumping down to a pressure of  $1 \times 10^{-4}$  mm is done three times, calculate the probable number of hydrogen molecules remaining:

$$x_3 = x_2 \times \left[ \frac{1 \times 10^{-4} \text{ mm}}{760 \text{ mm}} \right]^3$$

## CALCULATIONS INVOLVING GAS LAWS

**PROBLEM 15** A research worker isolated an unknown compound from one of his reaction products. This compound was a volatile liquid with a boiling point of 65°C. A 0.134-g sample of the liquid was vaporized and the gas was collected. The temperature of the collecting chamber was kept at 98°C in order that liquefaction would not occur. After all the sample was volatilized, the volume of the gas was measured as 53.2 ml at 98°C and 737 mm. Calculate the molecular weight.

	$m$	$V$	$T$	$P$
original	0.134 g	53.2 ml	371°K	737 mm
known	$m_2$	22.4 liters	273°K	760 mm

$$m_2 = 0.134 \text{ g} \times \frac{22.4 \text{ liters} \times 1000 \text{ ml}}{53.2 \text{ ml} \times 1 \text{ liter}} \times \frac{371^\circ\text{K}}{273^\circ\text{K}} \times \frac{760 \text{ mm}}{737 \text{ mm}}$$

(Note that  $m_2$  is expressed in grams. This is the weight of  $6.02 \times 10^{23}$  molecules. The molecular weight is the same number, but the units are atomic weight units.)

### A GENERAL GAS EQUATION

As previously stated (and as assumed in many of the problems in this chapter), there are four variable quantities that completely describe a given amount of a gas:  $m$ ,  $V$ ,  $T$ , and  $P$ . The amount of gas present can be expressed in terms of the number of moles,  $n$ , instead of the mass,  $m$ . For a sample of a gas, these variables do not change independently of one another. Indeed, if three of them are fixed, the other is also fixed.

The volume of a gas is directly proportional to the number of moles present,  $n$ , and to the absolute temperature  $T$ ; the volume is inversely proportional to the pressure  $P$ . Stated mathematically,

$$V \propto nT \frac{1}{P} \quad \text{or} \quad V = RnT \frac{1}{P}$$

where  $R$  is a constant of proportionality called the *ideal gas constant*. This equation is commonly written as

$$PV = nRT$$

and is called the *ideal gas law*.

If we consider 1 mole of a gas at STP,

$n$	$V$	$T$	$P$
1 mole	22.414 liters	273.15°K	1 atm

we can substitute values in the equation (as rearranged) and solve for  $R$ :

$$\begin{aligned} R &= \frac{VP}{Tn} = \frac{(22.414 \text{ liters})(1 \text{ atm})}{(273.15^\circ\text{K})(1 \text{ mole})} \\ &= 0.082057 \frac{\text{liter} \times \text{atm}}{^\circ\text{K} \times \text{mole}} \end{aligned}$$

Rounding this value to two significant figures gives

$$PV = n \cdot 0.082 T$$

Because the number of moles ( $n$ ) is equal to the weight of the gas being considered divided by the weight per mole, we may rewrite the above equation as follows:

$$PV = \frac{m}{\text{molar wt}} \cdot 0.082 T$$

In order to show the utility of the ideal gas law equations, the solutions to Problems 12 and 15 are restated below in terms of these equations. Because  $R$  has the units of (liter) (atm)/(°K) (mole), we must express all data in these units.

**PROBLEM 16** See statement of Problem 12.

*Solution*

$$PV = nRT$$

$$10 \text{ atm} \times 10 \text{ liters} = n \times 0.082 \frac{\text{liters} \times \text{atm}}{^\circ\text{K} \times \text{moles}} \times 300^\circ\text{K}$$

$$n = \frac{10 \times 10}{300 \times 0.082} \text{ moles}$$

$$\text{wt of O}_2 = \frac{10 \times 10}{300 \times 0.082} \text{ moles} \times \frac{32 \text{ g}}{1 \text{ mole}} = \frac{10 \times 10 \times 32}{300 \times 0.082} \text{ g}$$

**PROBLEM 17** See statement of Problem 15.

*Solution*

$$PV = \frac{m}{\text{molar wt}} RT$$

$$\frac{737}{760} \text{ atm} \times 0.0532 \text{ liter} = \frac{0.134 \text{ g}}{\text{molar wt}} \times 0.082 \frac{\text{liters} \times \text{atm}}{^\circ\text{K} \times \text{moles}} \times 371^\circ\text{K}$$

$$\text{molar wt} = \frac{0.134 \times 0.082 \times 760 \times 371}{737 \times 0.0532} \text{ g/mole}$$

## DEVIATIONS FROM GAS LAWS

Thus far in our discussion of the gas laws, there has been no indication that the various laws do not hold equally well for all gases and that they are not absolutely exact. Actually the gas laws are exact only when applied to what might be called an *ideal* gas. The molecules of such a gas would have no attraction for one another; nor would they occupy any space in the containing vessel (an impossible situation). However, real gases do not act in a completely ideal way; that is, their molecules do attract one another and they do take up some space. A given gas acts in a less ideal way:

1. As its pressure is increased. The molecules are forced closer

## CALCULATIONS INVOLVING GAS LAWS

together, thus increasing the effectiveness of the attractive forces and also increasing the proportion of the volume occupied by the molecules themselves.

2. *As its temperature is decreased.* The molecules have less kinetic energy, thus increasing the effectiveness of the attractive forces.

The amount of deviation from ideal gas behavior depends also on the gas. Gases like hydrogen, helium, nitrogen, and oxygen, whose molecules have relatively small attraction for one another, act more ideally at ordinary temperatures and pressures than do gases like carbon dioxide and ammonia, whose molecules have relatively great attraction for one another. For example, a mole of an ideal gas at  $0^{\circ}\text{C}$  and 760 mm has a volume of 22.414 liters. The actual volumes per mole of three common gases are:

hydrogen	22.43 liters
oxygen	22.393 liters
carbon dioxide	22.263 liters

Deviations such as these would introduce errors into the calculation of molecular weights by either the gas density method or the effusion method. Also, the amount of deviation between the actual molar volume of a gas and the value of 22.414 liters is a measure of the departure of a gas from ideal behavior. The more nearly ideal a gas, the more nearly it behaves as predicted by Boyle's law, Charles' law, and the other gas laws.

## CHAPTER REVIEW

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### *Terms*

Boyle's law, Charles' law, Dalton's law of partial pressures, Avogadro's law, STP, Graham's law of diffusion, relative molecular weights from gas densities, oxygen standard, carbon-12 standard, molar gas volume—22.4 liters, molecular weight from rate of effusion, mean free path, general gas equation, ideal gas constant, ideal gas, deviations from gas laws.

### *Exercises*

*Note that variables that are not mentioned in the statement of a problem—temperature in the case of Exercise 1—are assumed to be unchanged. For Exercise 1, knowing that a gas tends to become cooler as it expands, we assume that heat energy is added so that the final temperature is the same as the initial temperature.*

1. A sample of gas having a volume of 700 ml at a pressure of 3,200 mm is allowed to expand till the volume is 1,800 ml. Calculate the resulting pressure of the gas.
2. The pressure exerted by oxygen in a 1.0-liter container is 74 mm. What pressure does this same quantity of oxygen exert in a 5.0-liter container; in a 0.50-liter container?

3. What volume does a quantity of nitrogen measuring 100 ml at  $20^{\circ}\text{C}$  have at  $120^{\circ}\text{C}$ ; at  $-20^{\circ}\text{C}$ ?
4. Suppose a mineral oil with a vapor pressure equal to that of mercury and a density of 0.80 g/ml is available to fill barometer tubes. What would the minimum height of the tube need to be in order to measure a pressure difference of 1 atm?
5. A quantity of gas exerts a pressure of 3.0 atm when its volume is 1.0 liter at  $20^{\circ}\text{C}$ . What must be the size of container to confine the gas so that its pressure is 8.0 atm at  $20^{\circ}\text{C}$ ?
6. The pressure and volume of a quantity of hydrogen are 700 mm and 810 ml, respectively. What is the pressure of this quantity of hydrogen when it is confined in a 2.0-liter vessel?
7. A quantity of nitrogen has a volume of 1.0 qt at a pressure of 1.0 atm. What is the volume of this nitrogen at 0.90 psi; at 1,500 mm?
8. Convert the following temperatures to degrees absolute:  $35^{\circ}\text{C}$ ,  $35^{\circ}\text{F}$ ,  $-10^{\circ}\text{C}$ ,  $-10^{\circ}\text{F}$ .
9. Forty grams of argon has a volume of 22.4 liters at STP. Calculate the volume of this quantity of argon at  $27^{\circ}\text{C}$  and 900 mm.
10. A sample of carbon dioxide has a volume of 1.1 qt at  $68^{\circ}\text{F}$  and 20 psi. Calculate the volume of the  $\text{CO}_2$  in liters at STP.
11. To a 2-liter container of hydrogen at 3 atm are added 3 liters of nitrogen measured originally at 2 atm, 0.5 liter of oxygen measured originally at 1 atm, and 2 liters of sulfur dioxide measured originally at 3 atm. Calculate the partial pressure of each gas in the mixture. Calculate the total pressure.
12. A quantity of oxygen exerts a pressure of 3 atm. What is the pressure of one-third as much oxygen (by weight) occupying twice the volume at one-half the original absolute temperature?
13. The volume of a quantity of argon at  $1.0^{\circ}\text{C}$  is 10 ml. What is its volume at  $2.0^{\circ}\text{C}$ ; at  $-1.0^{\circ}\text{C}$ ; at  $1.0^{\circ}\text{K}$ ? How reliable is your last calculation?
14. A sample of carbon monoxide has a volume of 3.0 liters at  $27^{\circ}\text{C}$ . At what temperature does this sample have a volume of 4.0 liters?
15. Fourteen grams of nitrogen has a volume of 11.2 liters at  $32^{\circ}\text{F}$  and 14.7 psi. Calculate its volume at  $32^{\circ}\text{C}$  and 1,520 mm.
16. The gauge on a steel cylinder of hydrogen shows a pressure of 100 psi at  $27^{\circ}\text{C}$ . Calculate the pressure the gauge should show when each of the following changes is made:
  - a. The temperature is raised to  $127^{\circ}\text{C}$ .
  - b. The temperature is lowered to  $-73^{\circ}\text{C}$ .
  - c. A quantity of hydrogen equal to one-half of the weight of the original hydrogen is added while the temperature is held at  $27^{\circ}\text{C}$ .
  - d. A quantity of hydrogen equal to one-half of the weight of the original hydrogen is added. The temperature climbs to  $37^{\circ}\text{C}$  during the addition.

**CALCULATIONS INVOLVING  
GAS LAWS**

17. A quantity of oxygen, measured over water at 27°C and 727 mm, has a volume of 100 ml. Calculate the volume of the oxygen when dry at standard conditions.
18. A quantity of sulfur dioxide, measured over mercury at 27°C and 727 mm, has a volume of 100 ml. Calculate the volume at STP.
19. The weight of 1.0 liter of a certain gas is 2.0 g at 27°C and 700 mm. What is the weight of 100 ml of this gas measured at -13°C and 2,100 mm?
20. A quantity of neon exerts a pressure of 1,100 mm at 20°C in a 600-ml container. What is the pressure of this neon in a 1,400-ml container at 40°C?
21. A drop of water is added to a 500-ml flask filled with dry nitrogen at 35°C and 810 mm. After standing at 35°C till equilibrium is reached, what should be the gas pressure in the flask?
22. A quantity of nitrogen measured over water at 30°C and 730 mm has a volume of 110 ml. Calculate the volume of the nitrogen when dry at STP.
23. Calculate the volume of 0.10 mole of oxygen at STP; at 27°C and 700 mm; when measured over water at 27°C and 700 mm.
24. Calculate the molecular weight of the gaseous compound X if 10.0 g of X has a volume of 2.00 liters at STP. What is the weight of 1 mole of X; of  $6.02 \times 10^{23}$  molecules of X?
25. The volume of a sample of a new gaseous compound weighing 0.501 g was found to be 132 ml when measured over water at 26.0°C and 742 mm. Calculate the weight of 1 mole of the compound. What is its molecular weight?
26. What is the partial pressure of nitrogen in a mixture composed of 96 g of O<sub>2</sub> and 140 g of N<sub>2</sub>, the total pressure being 1,200 mm?
27. The partial pressures of carbon dioxide and methane in a mixture of the two in a 5.0-liter vessel are 4.5 atm and 6.2 atm, respectively, at 27°C. What is the weight of CH<sub>4</sub> in the vessel?
28. The density of X at STP is 2.1 g/liter. What is the molecular weight of X? How many molecules of X are present in 1 liter at STP?
29. Calculate the number of molecules in 1 liter of oxygen at 17°C and 780 mm. What is the number of molecules of helium in 1 liter under similar conditions?
30. The time required for a volume of X to effuse through a small hole was 84 sec. The time required for the same volume of nitrogen was 21 sec. Calculate the molecular weight of X.
31. Compare the mean free path of oxygen molecules at STP with that of oxygen under the following conditions: 0°C and 2 atm; 546°K and 1 atm; 1.0 liter containing 3.2 g.
32. Calculate the weight in grams of a CO<sub>2</sub> molecule.

33. Is the numerical value of the Avogadro number the same for both the carbon-12 and the oxygen scale of atomic weights? Explain. Is the calculated weight of a molecule in grams the same, irrespective of which scale is used? Explain.
34. Calculate the number of moles of helium in a 10-liter cylinder at 17°C and 21 atm.
35. Calculate the approximate weight of dry air (see Table 30-4) in an automobile tire, volume 3.0 gal, that has been inflated to a pressure of 28 psi above the prevailing air pressure. List the assumptions that you make as you proceed with the calculation.
36. Compare the rates of diffusion of the following pairs of gases:
  - a. Methane, CH<sub>4</sub>, and oxygen, O<sub>2</sub>
  - b. Nitrous oxide, N<sub>2</sub>O, and carbon dioxide, CO<sub>2</sub>
  - c. Sulfur dioxide, SO<sub>2</sub>, and helium, He
37. A 10-liter cylinder contains 35 g of sulfur dioxide, 30 g of methane, CH<sub>4</sub>, and 40 g of argon. What should be the pressure on the cylinder gauge at 0°C?
38. In which case should the measured molar volume at STP be more nearly equal to the ideal molar volume, for NH<sub>3</sub> or CH<sub>4</sub>; for Ar or He? Why?
39. Would you expect the density at STP calculated from the formula of hydrogen chloride to be larger or smaller than the measured density? Explain.
40. In an effusion apparatus, 0.0010 mole of oxygen at 760 mm was found to effuse in 5.1 min at 27°C. What volume of methane, CH<sub>4</sub>, effuses from this apparatus in the same period of time? What volume of methane effuses if the temperature is 10°C higher than for the oxygen effusion?
41. A sample of ethane (C<sub>2</sub>H<sub>6</sub>) weighing 1.0 g is passed through water and collected in a flask at 17°C. If the volume of the gas collected is 740 ml, what is the pressure of the gas?
42. On a certain day the atmospheric pressure in Boone, North Carolina, was 682 mm. In a normal breath of 1.4 liters, approximately how many molecules of oxygen did a Boone resident inhale? How many molecules would one inhale if the pressure were 740 mm?
43. Would you predict that the number of CO<sub>2</sub> molecules in 22.414 liters is more than  $6.023 \times 10^{23}$ ? Explain.
44. Both X and Y are gases at room temperature. Their critical temperatures are -60°C and 80°C, respectively.
  - a. At room temperature, both effuse through a tiny hole at approximately the same rate (Y is slightly faster). What can be deduced from this information?
  - b. Which is more likely to behave as an ideal gas at STP? Explain.
  - c. Can either be liquefied at room temperature by the application of pressure?
  - d. The molecules of which would have the higher kinetic energy at 20°C?
  - e. Which is more likely to be composed of polar molecules? Explain.



**CALCULATIONS INVOLVING  
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**SUPPLEMENTARY READING**

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- Dampier, W. C., and M. Dampier: *Readings in the Literature of Science*, Harper & Row, Publishers, Incorporated, New York, 1959, pp. 105-111.
- Nash, L. K.: *The Atomic-Molecular Theory, Harvard Case Histories in Science, Case 4*, Harvard University Press, Cambridge, Mass., 1950.
- Neville, R. G.: "The Discovery of Boyle's Law, 1661-62," *J. Chem. Educ.*, **39**: 356 (1962).

# CALCULATIONS

## INVOLVING FORMULAS

## AND EQUATIONS



In Chap. 1 we discussed the law of definite composition, one of the most fundamental and useful laws of chemistry. In this chapter we consider several types of calculations, all of which, at least in part, are based on this law.

### CALCULATIONS BASED ON FORMULAS

#### PERCENTAGE COMPOSITION OF COMPOUNDS

The weights of the elements comprising a mole of a compound are readily deduced from the formula of the compound and the atomic weights of the elements. The percentage composition by weight is then calculated from the weights of the elements and the weight of a mole of the compound.

**PROBLEM 1** Calculate the per cent by weight of each element in magnesium chloride,  $\text{MgCl}_2$ .

*Solution* In 1 mole of  $\text{MgCl}_2$  there are 1 mole of  $\text{Mg}^{2+}$  ions and 2 moles of  $\text{Cl}^-$  ions. The weights of these ions and the weight of 1 mole of the compound are:

$$\begin{aligned}\text{wt of } \text{Mg}^{2+} &= 1 \text{ mole} \times 24.31 \text{ g/mole} = 24.3 \text{ g} \\ \text{wt of } \text{Cl}^- &= 2 \text{ moles} \times 35.45 \text{ g/mole} = \underline{70.9 \text{ g}} \\ \text{wt of 1 mole of } \text{MgCl}_2 &= \underline{95.2 \text{ g}}\end{aligned}$$

Note that the calculated weights have been rounded to three significant figures. See the Appendix for a discussion of significant figures.

The percentages by weight are then calculated as follows:

$$\text{magnesium: } \frac{24.3 \text{ g}}{95.2 \text{ g}} \times 100 = 25.5 \text{ per cent}$$

## CALCULATIONS INVOLVING FORMULAS AND EQUATIONS

$$\text{chlorine: } \frac{70.9 \text{ g}}{95.2 \text{ g}} \times 100 = 74.5 \text{ per cent}$$

*Check* Chlorine atoms are about  $1\frac{1}{2}$  times as heavy as magnesium atoms, and there are 2 times as many of the former in a sample of  $\text{MgCl}_2$ . Hence, we would expect the weight due to chlorine to be about 3 times the weight due to magnesium, that is, 3 parts out of 4, or about 75 per cent.

It is interesting to note that the percentages that we have calculated are not those of a single  $\text{MgCl}_2$  unit, because no single ion of  $\text{Mg}^{2+}$  has a mass of 24.31 awu and no single ion of  $\text{Cl}^-$  has a mass of 35.45 awu. However, any natural sample of  $\text{MgCl}_2$  that we could weigh, even with the most sensitive analytical balance, would have this composition, because it would be composed of atoms of all the natural isotopes.

**PROBLEM 2** Calculate the percentage composition by weight of ether,  $(\text{C}_2\text{H}_5)_2\text{O}$ .

*Solution*

$$\text{wt due to C} = 4 \text{ moles} \times 12.0 \text{ g/mole} = 48.0 \text{ g}$$

$$\text{wt due to H} = 10 \text{ moles} \times 1.01 \text{ g/mole} = 10.1 \text{ g}$$

$$\text{wt due to O} = 1 \text{ mole} \times 16.0 \text{ g/mole} = 16.0 \text{ g}$$

$$\text{wt of 1 mole of ether:} \quad \quad \quad 74.1 \text{ g}$$

$$\text{per cent by wt of C} = \frac{48.0 \text{ g}}{74.1 \text{ g}} \times 100 = 64.8 \text{ per cent}$$

$$\text{per cent by wt of H} = \frac{10.1 \text{ g}}{74.1 \text{ g}} \times 100 = 13.6 \text{ per cent}$$

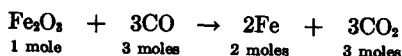
$$\text{per cent by wt of O} = \frac{16.0 \text{ g}}{74.1 \text{ g}} \times 100 = 21.6 \text{ per cent}$$

$$\text{total} \quad \quad \quad 100.0 \text{ per cent}$$

*Check* The percentages add to 100 per cent (frequently in other examples to 99.9, 99.8, 100.1, or something close to 100, depending on how fractions have been rounded). However, this is not a complete check, because mistakes may have been made in calculating the weights of moles of elements or of compound. There are 4/10 as many carbon atoms as hydrogen atoms, and the former weighs 12 times the latter. Hence, we would expect the weight of carbon to be  $\frac{48}{10}$  or about 5 times the weight of hydrogen. The calculated percentages are in the ratio of about 5:1 (64.8 per cent C and 13.6 per cent H). The weight of oxygen is  $\frac{16}{10}$  or about  $1\frac{1}{2}$  times the weight of hydrogen. The calculated percentages are in this ratio.

## WEIGHT RELATIONSHIPS IN CHEMICAL REACTIONS

Consider a chemical reaction such as the reduction of iron(III) oxide with carbon monoxide. If the formulas for reactants and products are known, a balanced equation can be written for the chemical reaction.



From the balanced equation it is seen that 3 moles of carbon monoxide is required to reduce 1 mole of iron(III) oxide and that 2 moles of iron and 3 moles of carbon dioxide are formed. Because the molar weights are obtainable from the atomic weights, the weight relationship between reactants and products for this, or any other chemical reaction that we can represent with an equation, is easily established.

**PROBLEM 3** Calculate the weight of iron that results when 16.0 g of  $\text{Fe}_2\text{O}_3$  is reduced with CO. What weight of CO is required for the reduction? What weight of  $\text{CO}_2$  is formed?

*Solution* The first step in the solution of this type of problem is to calculate the number of moles of reactants available for the reaction. Only 16.0 g of  $\text{Fe}_2\text{O}_3$  is to react, and so let us calculate the number of moles in this amount. By adding the atomic weights (rounded to three significant figures), we find the weight of one  $\text{Fe}_2\text{O}_3$  unit to be 160 awu. The weight of 1 mole of  $\text{Fe}_2\text{O}_3$  is therefore 160 g:

$$\begin{aligned} \text{moles of Fe}_2\text{O}_3 \text{ in } 16.0 \text{ g} &= 16.0 \text{ g of Fe}_2\text{O}_3 \times \frac{1 \text{ mole of Fe}_2\text{O}_3}{160 \text{ g of Fe}_2\text{O}_3} \\ &= 0.100 \text{ mole of Fe}_2\text{O}_3 \end{aligned}$$

We are now ready to calculate the number of moles of the other reactant (CO) and of the products (Fe and  $\text{CO}_2$ ). Refer again to the equation for the reaction. The equation states that for 1 mole of  $\text{Fe}_2\text{O}_3$  3 moles of CO are required and that 2 moles of Fe and 3 moles of  $\text{CO}_2$  will be produced:

$$\text{moles of CO} = 0.100 \text{ mole of Fe}_2\text{O}_3 \times \frac{3 \text{ moles of CO}}{1 \text{ mole of Fe}_2\text{O}_3} = 0.300 \text{ mole of CO}$$

$$\text{moles of Fe} = 0.100 \text{ mole of Fe}_2\text{O}_3 \times \frac{2 \text{ moles of Fe}}{1 \text{ mole of Fe}_2\text{O}_3} = 0.200 \text{ mole of Fe}$$

$$\text{moles of CO}_2 = 0.100 \text{ mole of Fe}_2\text{O}_3 \times \frac{3 \text{ moles of CO}_2}{1 \text{ mole of Fe}_2\text{O}_3} = 0.300 \text{ mole of CO}_2$$

We have calculated that, when 0.100 mole (16.0 g) of  $\text{Fe}_2\text{O}_3$  is reduced, 0.300 mole of CO is used, and 0.200 mole of Fe and 0.300 mole of  $\text{CO}_2$  are produced. To find the weights of these quantities, we make use of the weight of a mole of each compound:

$$\text{wt of CO required} = 0.300 \text{ mole of CO} \times \frac{28 \text{ g of CO}}{1 \text{ mole of CO}} = 8.4 \text{ g of CO}$$

$$\text{wt of Fe produced} = 0.200 \text{ mole of Fe} \times \frac{55.8 \text{ g of Fe}}{1 \text{ mole of Fe}} = 11.2 \text{ g of Fe}$$

$$\text{wt of CO}_2 \text{ produced} = 0.300 \text{ mole of CO}_2 \times \frac{44.0 \text{ g of CO}_2}{1 \text{ mole of CO}_2} = 13.2 \text{ g of CO}_2$$

*Check*

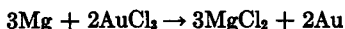
$$\text{wt of reactants} = \text{wt of products}$$

$$16.0 \text{ g of Fe}_2\text{O}_3 + 8.4 \text{ g of CO} = 11.2 \text{ g of Fe} + 13.2 \text{ g of CO}_2$$

$$24.4 \text{ g of reactants} = 24.4 \text{ g of products}$$

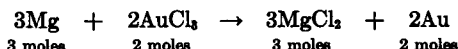
# CALCULATIONS INVOLVING FORMULAS AND EQUATIONS

**PROBLEM 4** The equation for the reaction between elemental magnesium and a solution of gold(III) chloride is



If a piece of magnesium weighing 1.00 g is placed in a solution that contains 3.00 g of gold(III) chloride dissolved in water, which of the reactants is present in excess? What weight of gold (Au) is formed? How much of the excess reactant is left when the reaction is over?

*Solution* From the balanced equation we get the mole ratios of reactants and products:



Calculation of the number of moles of each reactant available:

$$\text{moles of Mg} = 1.00 \text{ g of Mg} \times \frac{1 \text{ mole of Mg}}{24.3 \text{ g of Mg}} = 0.0412 \text{ mole of Mg}$$

$$\text{moles of AuCl}_3 = 3.00 \text{ g of AuCl}_3 \times \frac{1 \text{ mole}}{303 \text{ g of AuCl}_3} = 0.00990 \text{ mole of Au}$$

It is seen from the equation that, if 0.0412 mole of Mg reacts, 0.0412  $\times$   $\frac{2}{3}$  mole or 0.0274 mole of AuCl<sub>3</sub> must be present to react with it. However, there is only 0.00990 mole of AuCl<sub>3</sub>, so that not all the magnesium can react. That is, the magnesium is present in excess.

Because all the AuCl<sub>3</sub> can react, we base our calculations of actual reactants and products on the amount of gold(III) chloride present and not on the amount of magnesium:

$$\begin{aligned} \text{moles of Au formed} &= 0.00990 \text{ mole of AuCl}_3 \times \frac{2 \text{ moles of Au}}{2 \text{ moles of AuCl}_3} \\ &= 0.00990 \text{ mole of Au} \end{aligned}$$

$$\text{wt of Au formed} = 0.00990 \text{ mole of Au} \times \frac{197 \text{ g of Au}}{1 \text{ mole of Au}} = 1.92 \text{ g of Au}$$

$$\begin{aligned} \text{moles of Mg that react} &= 0.00990 \text{ mole of AuCl}_3 \times \frac{3 \text{ moles of Mg}}{2 \text{ moles of AuCl}_3} \\ &= 0.0148 \text{ mole of Mg} \end{aligned}$$

$$\begin{aligned} \text{moles of Mg left in excess} &= 0.0412 \text{ mole of Mg} - 0.0148 \text{ mole of Mg} \\ &= 0.0264 \text{ mole of Mg} \end{aligned}$$

$$\text{wt of Mg left in excess} = 0.0264 \text{ mole} \times \frac{24.3 \text{ g of Mg}}{1 \text{ mole of Mg}} = 0.642 \text{ g of Mg}$$

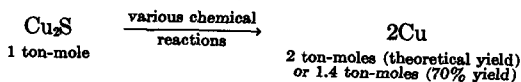
*Check* Gold atoms are about 8 times heavier than magnesium atoms. However only  $\frac{2}{3}$  as many gold atoms are formed. The weight of gold formed is about  $8 \times \frac{2}{3}$  or 5 times the weight of the magnesium that reacts (1.94 g of gold is about 5 times as heavy as 1.00 g — 0.64 g = 0.36 g of magnesium).

**THEORETICAL YIELD.** In solving the two preceding problems, it was assumed that the reactions proceeded so that all the reactants were converted to the products shown in the equations. This seldom happens

in actual practice, because many reactions do not "go to completion" but end in an equilibrium state with appreciable quantities of reactants and products present. Also, the reactants may react in a manner to form two or more sets of products, so that a single equation does not tell the whole story about a chemical reaction. Frequently, too, in separating and purifying the products of a chemical reaction, some of the product is lost. The weights that we calculated in Problems 2 and 3 are the *theoretical weights* or *theoretical yields*; in actual practice the recovery of product is less than 100 per cent, sometimes much less.

**PROBLEM 5** A certain copper ore contains an average 2.0 per cent  $\text{Cu}_2\text{S}$ . The metallurgical processes for recovering elemental copper from this ore give a 70 per cent yield of the theoretical. What weight of copper is recovered from 100 tons of ore?

*Solution* With the weight of the ore given in tons, it is convenient to use *ton-moles* for our comparative quantities:



The weight of a ton-mole is simply the weight of a formula unit expressed in tons. A ton-mole of  $\text{Cu}_2\text{S}$  weighs 159.14 tons, and a ton-mole of Cu weighs 63.54 tons. Because only two significant figures are used in specifying the composition of the ore and the percentage yield, these figures can be rounded to 160 and 64 tons, respectively:

$$\begin{aligned} \text{wt of Cu}_2\text{S available} &= 100 \text{ tons of ore} \times \frac{0.020 \text{ tons of Cu}_2\text{S}}{1 \text{ ton of ore}} \\ &= 2.0 \text{ tons of Cu}_2\text{S} \end{aligned}$$

$$\begin{aligned} \text{moles of Cu}_2\text{S available} &= 2.0 \text{ tons} \times \frac{1 \text{ ton-mole of Cu}_2\text{S}}{160 \text{ tons}} \\ &= 0.012 \text{ ton-mole of Cu}_2\text{S} \end{aligned}$$

$$\begin{aligned} \text{moles of Cu (70\% yield)} &= 0.012 \text{ ton-mole of Cu}_2\text{S} \times \frac{1.4 \text{ ton-mole of Cu}}{1 \text{ ton-mole of Cu}_2\text{S}} \\ &= 0.017 \text{ ton-mole of Cu} \end{aligned}$$

$$\begin{aligned} \text{wt of Cu (70\% yield)} &= 0.017 \text{ ton-mole of Cu} \times \frac{64 \text{ tons of Cu}}{1 \text{ ton mole}} \\ &= 1.1 \text{ tons of Cu} \end{aligned}$$

*Check* For the remainder of the chapter, we leave the responsibility of studying the answers to the problems to the student to see if they appear reasonably correct. It is not uncommon for a student to work a problem similar to number 5 on a test, and submit an answer like 11 or even 1,100 tons of Cu. Even a casual check would reveal the impossibility of such answers.

## WEIGHT-VOLUME RELATIONSHIPS

The volume of a mole of any gas measured at STP is 22.4 liters. This relationship is the basis for calculating the volumes of gaseous reactants and products involved in chemical reactions. If a volume is

## CALCULATIONS INVOLVING FORMULAS AND EQUATIONS

specified at some temperature and pressure other than STP, corrections are made by means of Boyle's and Charles' laws.

**PROBLEM 6** Calculate the volume of hydrogen and of oxygen theoretically obtainable by the decomposition of 100 g of water by electrolysis.

*Solution* To solve this problem, we first write a balanced chemical equation and calculate the number of moles of hydrogen and oxygen that are formed from the decomposition of 100 g of water. This procedure is exactly like the solutions to the problems discussed in the previous section:

$$\begin{array}{c}
 \begin{array}{ccc}
 2\text{H}_2\text{O} & \xrightarrow{\text{elec.}} & 2\text{H}_2 & + & \text{O}_2 \\
 \text{2 moles} & & \text{2 moles} & & \text{1 mole}
 \end{array} \\
 \text{moles of water} = 100 \text{ g of H}_2\text{O} \times \frac{1 \text{ mole of H}_2\text{O}}{18.0 \text{ g}} = \frac{100}{18.0} \text{ moles of H}_2\text{O} \\
 \text{moles of H}_2 = \frac{100}{18.0} \text{ moles of H}_2\text{O} \times \frac{2 \text{ moles of H}_2}{2 \text{ moles of H}_2\text{O}} = \frac{100}{18.0} \text{ moles of H}_2 \\
 \text{moles of O}_2 = \frac{100}{18.0} \text{ moles of H}_2\text{O} \times \frac{1 \text{ mole of O}_2}{2 \text{ moles of H}_2\text{O}} = \frac{100}{36.0} \text{ moles of O}_2 \\
 \text{vol of H}_2 = \frac{100}{18.0} \text{ moles of H}_2 \times \frac{22.4 \text{ liters of H}_2}{1 \text{ mole of H}_2} = 124 \text{ liters of H}_2 \text{ at STP} \\
 \text{vol of O}_2 = \frac{100}{36.0} \text{ moles of O}_2 \times \frac{22.4 \text{ liters of O}_2}{1 \text{ mole of O}_2} = 62 \text{ liters of O}_2 \text{ at STP}
 \end{array}$$

**PROBLEM 7** If 100 g of water is decomposed (see Problem 6), what volumes are obtained of hydrogen and oxygen if the gases are collected at 700 mm and 26°C?

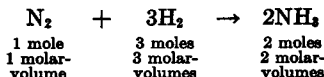
*Solution*

$$\begin{aligned}
 \text{vol of H}_2 &= \frac{100}{18.0} \text{ moles of H}_2 \times \frac{22.4 \text{ liters of H}_2}{1 \text{ mole of H}_2} \times \frac{760 \text{ mm}}{700 \text{ mm}} \times \frac{299^\circ\text{K}}{273^\circ\text{K}} \\
 &= 148 \text{ liters of H}_2
 \end{aligned}$$

vol of O<sub>2</sub> = one-half the volume of H<sub>2</sub>, or 74 liters

**PROBLEM 8** What is the theoretical volume of ammonia formed by the action of 10 liters of hydrogen with nitrogen? What volume of nitrogen reacts? (All volumes are measured at the same temperature and pressure.)

*Solution*



We could proceed here as in Problem 7 by first calculating the number of moles of ammonia and of nitrogen and then multiplying the number of moles of each by liters per mole, that is, 22.4 liters/mole. However, a more direct approach can be followed, because the volume of H<sub>2</sub> is given in the problem rather than its weight. Because equal volumes contain the same number of molecules (Avogadro's law), the volume of the nitrogen is one-third the volume of H<sub>2</sub>. This follows from the balanced equation that states that one molecule of N<sub>2</sub> reacts with three molecules of H<sub>2</sub>. From the same line of reasoning, we see that the volume of NH<sub>3</sub> is two-thirds that of H<sub>2</sub>.

$$\text{vol of NH}_3 \text{ formed} = 10 \text{ liters of H}_2 \times \frac{2 \text{ vol of NH}_3}{3 \text{ vol of H}_2} = 6.7 \text{ liters of NH}_3$$

$$\text{vol of N}_2 \text{ that reacts} = 10 \text{ liters of H}_2 \times \frac{1 \text{ vol of N}_2}{3 \text{ vol of H}_2} = 3.3 \text{ liters of N}_2$$

**Gay-Lussac's Law of Combining Volumes.** In 1805 and shortly thereafter, J. L. Gay-Lussac performed a series of experiments that showed that *gases react with one another in small, whole-numbered ratios by volume if the volumes are measured at the same temperature and pressure.* In the problem that we have just discussed, the volume ratio is nitrogen:hydrogen:ammonia = 1:3:2. Gay-Lussac's empirical law was an important contribution in the development of the science of chemistry, because it provided part of the background that enabled Avogadro, in 1811, to hypothesize that equal volumes of gases contain the same number of molecules.

## EQUIVALENT WEIGHTS

As the name implies, equivalent weights are the amounts of substances that are equivalent to one another in chemical reactions. For example, 40.0 g of NaOH reacts with or is equivalent to 49 g of H<sub>2</sub>SO<sub>4</sub> or 36.5 g of HCl. Or 49 g of H<sub>2</sub>SO<sub>4</sub> is equivalent to 36.5 g of HCl in acid-base reactions, for these quantities neutralize the same weight of a base.

Equivalent weights are now defined in terms of Avogadro's number. The *equivalent weight* of an acid is the weight in grams that donates  $6.02 \times 10^{23}$  protons; the equivalent weight of a base is the weight in grams that accepts  $6.02 \times 10^{23}$  protons. For oxidation-reduction reactions, if a substance acts as an oxidizing agent, the weight in grams that will accept  $6.02 \times 10^{23}$  electrons is called its equivalent weight; if it acts as a reducing agent, the weight in grams that supplies this number of electrons is the equivalent weight.<sup>1</sup> The relationship between the weight of a mole and the equivalent weight for several substances is shown in Tables 9-1 and 9-2. In some texts, the term *gram-equivalent weight* is used to signify that the weight is expressed in grams. We shall use the same plan that we have been using with the term mole; that is, it is understood that the weight of a mole or an equivalent weight is expressed in grams unless otherwise indicated. The equivalent weight may also be called *combining weight* in the case of elements.

Equivalent weights are often calculated easily, as we can see in Table 9-2. Consider sodium. In most of its chemical reactions, a sodium atom gives up one electron to form the Na<sup>+</sup> ion. Hence, 1 mole,  $6.02 \times 10^{23}$  atoms, is required to supply  $6.02 \times 10^{23}$  electrons. The

<sup>1</sup> Instead of speaking of the loss or gain of electrons in this definition, we could speak of the increase or decrease in oxidation state, as we did in defining oxidation and reduction in Chap. 6.



# CALCULATIONS INVOLVING FORMULAS AND EQUATIONS

equivalent weight of sodium equals its molar weight. Consider aluminum. One aluminum atom gives up three electrons to form an  $\text{Al}^{3+}$  ion. Only one-third of a mole of Al atoms is required to give up  $6.02 \times 10^{23}$  electrons. The equivalent weight of aluminum is one-third of its molar weight. Consider oxygen. One oxygen atom gains two electrons to form an  $\text{O}^{2-}$  ion. One-half of a mole of oxygen atoms is needed to accept  $6.02 \times 10^{23}$  electrons. The equivalent weight of oxygen is one-half of the weight of a mole of oxygen atoms. The same line of reasoning applies to the calculation of equivalent weights of acids and bases, as shown in Table 9-1. For example, because each  $\text{H}_2\text{SO}_4$  molecule may

TABLE 9-1 *Equivalent weights of acids and bases*

substance	weight of 1 mole, g	equivalent weight, g
hydrochloric acid, $\text{HCl}$	36.5	36.5
sulfuric acid, $\text{H}_2\text{SO}_4$	98.1	49.0
phosphoric acid, $\text{H}_3\text{PO}_4$	98.0	32.7
sodium hydroxide, $\text{NaOH}$	40.0	40.0
calcium hydroxide, $\text{Ca(OH)}_2$	74.1	37.0

donate two protons, only one-half of a mole is needed to donate  $6.02 \times 10^{23}$  protons. The equivalent weight of sulfuric acid is one-half of its molar weight. In the case of  $\text{HCl}$ , a mole is required for  $6.02 \times 10^{23}$  protons, so that the equivalent weight equals the molar weight. It follows that commonly the equivalent weight of any substance is either equal to the weight of a mole or is a whole-numbered fraction ( $\frac{1}{2}$ ,  $\frac{1}{3}$ ,  $\frac{2}{3}$ , etc.) of the weight of a mole.

A substance may have more than one equivalent weight. Iron, for example, in certain reactions may change from  $\text{Fe}$  to  $\text{Fe}^{2+}$  by giving up two electrons per atom. In this case the equivalent weight is one-half of the weight of a mole; or in other reactions iron may change from  $\text{Fe}$  to  $\text{Fe}^{3+}$ , in which case the equivalent weight is one-third of the weight of a mole; or  $\text{Fe}^{2+}$  may undergo a one-electron change to  $\text{Fe}^{3+}$ , in which case the equivalent weight and the weight of a mole of  $\text{Fe}^{2+}$  ions are the same (see Table 9-2).

TABLE 9-2 *Equivalent weights of oxidizing and reducing agents*

substance	weight of 1 mole of atoms, g	reaction	equivalent weight of atoms or ions, g
hydrogen	1.01	$\text{H} \rightarrow \text{H}^+ + \text{e}^-$	1.01
sodium	23.0	$\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$	23.0
aluminum	27.0	$\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$	9.0
iron	55.8	$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$	27.9
		$\text{Fe} \rightarrow \text{Fe}^{3+} + 3\text{e}^-$	18.6
		$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$	55.8
chlorine	35.5	$\text{Cl} + \text{e}^- \rightarrow \text{Cl}^-$	35.5
oxygen	16.0	$\text{O} + 2\text{e}^- \rightarrow \text{O}^{2-}$	8.0

**PROBLEM 9** What weight of calcium hydroxide is needed to neutralize 28.0 g of hydrochloric acid? What weight of phosphoric acid would this weight of calcium hydroxide neutralize?

*Solution*

$$\begin{aligned}\text{no. of equiv. wt of HCl} &= 28.0 \text{ g HCl} \times \frac{1 \text{ equiv. wt HCl}}{36.5 \text{ g HCl}} \\ &= 0.767 \text{ equiv. wt HCl}\end{aligned}$$

Because the number of equivalent weights of one reactant equals that of the other,

$$\text{no. of equiv. wt of Ca(OH)}_2 = 0.767 \text{ equiv. wt Ca(OH)}_2$$

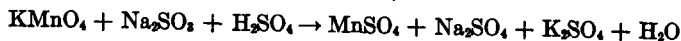
$$\begin{aligned}\text{wt of Ca(OH)}_2 \text{ needed} &= 0.767 \text{ equiv. wt Ca(OH)}_2 \times \frac{37.0 \text{ g Ca(OH)}_2}{1 \text{ equiv. wt Ca(OH)}_2} \\ &= 28.4 \text{ g Ca(OH)}_2 \text{ needed to neutralize 28.0 g HCl}\end{aligned}$$

Because the number of equivalents of phosphoric acid equals the number of equivalents of calcium hydroxide neutralized, or 0.767,

$$\begin{aligned}\text{wt of H}_3\text{PO}_4 \text{ neutralized} &= 0.767 \text{ equiv. wt H}_3\text{PO}_4 \times \frac{32.7 \text{ g H}_3\text{PO}_4}{1 \text{ equiv. wt H}_3\text{PO}_4} \\ &= 25.1 \text{ g H}_3\text{PO}_4 \text{ needed to neutralize 28.0 g Ca(OH)}_2\end{aligned}$$

From these calculations we see that 25.1 g of  $\text{H}_3\text{PO}_4$  is equivalent in reactivity as an acid to 28.0 g of HCl.

**PROBLEM 10** Calculate the weight of potassium permanganate,  $\text{KMnO}_4$ , necessary to oxidize 10 g of sodium sulfite,  $\text{Na}_2\text{SO}_3$ , to sodium sulfate. The oxidation is carried out in sulfuric acid solution with the following reactants and products (the equation is not balanced):



*Solution* By assigning oxidation numbers to each element in each reactant or product, we discover that only two elements change in oxidation number in the reaction. The manganese changes from an oxidation state of +7 in  $\text{KMnO}_4$  to +2 in  $\text{MnSO}_4$ , and the sulfur changes from +4 in  $\text{Na}_2\text{SO}_3$  to +6 in  $\text{Na}_2\text{SO}_4$ , or in whatever  $\text{SO}_4^{2-}$  compound it becomes part of.

We calculate the equivalent weights of  $\text{KMnO}_4$  and of  $\text{Na}_2\text{SO}_3$  on the basis of the changes in oxidation number of manganese and sulfur, respectively. The change in oxidation number for manganese from +7 to +2 is 5; hence, the equivalent weight of  $\text{KMnO}_4$  is one-fifth of the weight of a mole.

The change in oxidation number of sulfur from +4 to +6 is 2; hence, the equivalent weight of  $\text{Na}_2\text{SO}_3$  is one-half of the weight of a mole:

	weight of a mole	equivalent weight
$\text{KMnO}_4$	158 g	$1/5 (158 \text{ g}) = 32 \text{ g}$
$\text{Na}_2\text{SO}_3$	126 g	$1/2 (126 \text{ g}) = 63 \text{ g}$

$$\begin{aligned}\text{no. of equiv. wt of Na}_2\text{SO}_3 \text{ reacted} &= 10 \text{ g Na}_2\text{SO}_3 \times \frac{1 \text{ equiv. wt Na}_2\text{SO}_3}{63 \text{ g Na}_2\text{SO}_3} \\ &= \frac{10}{63} \text{ equiv. wt Na}_2\text{SO}_3\end{aligned}$$

## CALCULATIONS INVOLVING FORMULAS AND EQUATIONS

Because the number of equivalent weights of one reactant equals that of the other,

$$\text{no. of equiv. wt of KMnO}_4 = \frac{10}{63} \text{ equiv. wt KMnO}_4$$

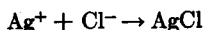
$$\begin{aligned} \text{wt of KMnO}_4 &= \frac{10}{63} \text{ equiv. wt KMnO}_4 \times \frac{32 \text{ g KMnO}_4}{1 \text{ equiv. wt KMnO}_4} \\ &= 5.1 \text{ g of KMnO}_4 \text{ to oxidize 10 g of Na}_2\text{SO}_3 \end{aligned}$$

*Alternate Solution* The weight of  $\text{KMnO}_4$  needed to oxidize 10 g of  $\text{Na}_2\text{SO}_3$  can be calculated on the basis of a balanced chemical equation, using the method illustrated in Problems 3 and 4 in this chapter. The balancing of complex oxidation-reduction reactions is taken up in Chap. 18. For the reaction in this problem, the balanced equation is



**PROBLEM 11** Eight-tenths of a gram of sodium chloride,  $\text{NaCl}$ , is required to precipitate the silver ions in a solution. If aluminum chloride,  $\text{AlCl}_3$ , had been used as the precipitating agent, what weight would have been required?

*Solution* In either case, the reaction is



Because the chloride ions are the reacting ions, we define the equivalent weight of the precipitating reactant as the weight that contains  $6.02 \times 10^{23}$   $\text{Cl}^-$  ions:

precipitating reactant	weight of a mole	equivalent weight
$\text{NaCl}$	58 g	58 g
$\text{AlCl}_3$	133 g	44 g

$$\begin{aligned} \text{no. of equiv. wt of NaCl} &= 0.8 \text{ g of NaCl} \times \frac{1 \text{ equiv. wt NaCl}}{58 \text{ g NaCl}} \\ &= \frac{0.8}{58} \text{ equiv. wt of NaCl} \end{aligned}$$

$$\text{no. of equiv. wt of AlCl}_3 = \frac{0.8}{58} \text{ (same as for NaCl)}$$

$$\text{wt of AlCl}_3 = \frac{0.8}{58} \text{ equiv. wt of AlCl}_3 \times \frac{44 \text{ g}}{1 \text{ equiv. wt}} = 0.6 \text{ g AlCl}_3$$

## CALCULATION OF FORMULAS FROM EXPERIMENTAL DATA

In the preceding section, we saw that the formula of a compound can be the source of much quantitative information about the compound. From the formula we can calculate the molecular weight, the molar weight, the percentage composition by weight, and the weight relationships in chemical reactions. Logically, however, this is putting the cart before the horse, because the formula for a compound cannot be known till the molecular weight and the percentage composition by weight have been determined experimentally. Even for the simple

compounds carbon dioxide and water, in order that we might have their useful formulas, someone had to go into the laboratory and determine experimentally (1) the elements that compose these compounds, (2) the percentages by weight of the elements in each, and (3) the relative molecular weight of each. In the remainder of this chapter, we shall discuss briefly how the composition of a compound is determined and how the formula is deduced from the experimental data.

A topic which we shall not discuss here but which was of the greatest significance in the early development of formulas is the determination of a standard scale of atomic weights. Definite relative weights must be assigned to the atoms of elements before the formula of a compound can be written. In Chap. 1, the early method used by Dalton and his contemporaries, based on experimental combining weights, was mentioned, and in Chap. 2, the modern mass spectrographic method for determining relative atomic weights was described. In the discussions that follow, it is assumed that a table of atomic weights is available.

### COMPOSITION OF NEW COMPOUNDS

Although the number of known compounds is probably in the range of 2 or 3 million, it is estimated that 100,000 new compounds are synthesized each year in the university and industrial research laboratories of the world. As these new compounds are obtained, their compositions must be experimentally determined. This is the first step in arriving at their formulas.

There are many methods for determining the percentage by weight of the different elements in a compound. These methods vary, depending on the nature of the compound and the elements in it. For instance, if a substance contains carbon and hydrogen, a weighed sample of the compound can be burned in a closed tube in a stream of oxygen to form carbon dioxide and water (Fig. 9-1). The combustion products

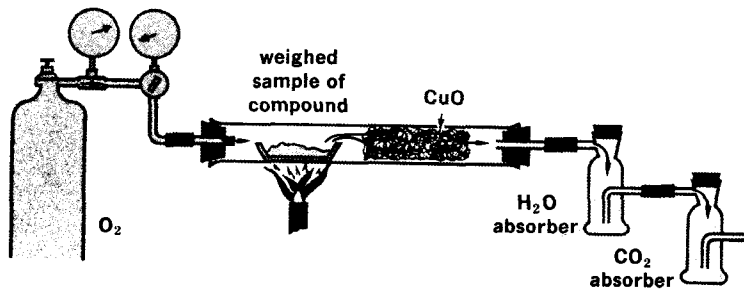


FIG. 9-1

Apparatus for determining the percentage of carbon and hydrogen in a compound. Copper oxide serves to oxidize traces of C, CO, and  $H_2$  to  $CO_2$  and  $H_2O$ .

## CALCULATIONS INVOLVING FORMULAS AND EQUATIONS

are swept from the tube by the stream of oxygen into two absorbing chemicals, one of which absorbs water vapor and the other carbon dioxide.

The gain in weight of each of the absorbers gives the weight of water and carbon dioxide, respectively. Because water is known to be  $\frac{2}{18}$  hydrogen by weight,  $\frac{2}{18}$  of the weight of the water is equal to the amount of hydrogen originally present in the compound. Similarly,  $\text{CO}_2$  is  $\frac{12}{44}$  carbon, and therefore  $\frac{12}{44}$  of the weight gained by the  $\text{CO}_2$  absorber is the weight of the carbon originally present in the sample. Then:

$$\% \text{ H} = \frac{\text{weight of hydrogen}}{\text{weight of sample}} \times 100$$

$$\% \text{ C} = \frac{\text{weight of carbon}}{\text{weight of sample}} \times 100$$

When nitrogen is present in a compound, a common way of finding its percentage is to decompose the compound by heating. The elemental nitrogen thus formed is swept out of the apparatus by carbon dioxide and collected over aqueous  $\text{NaOH}$  (Fig. 9-2). The carbon

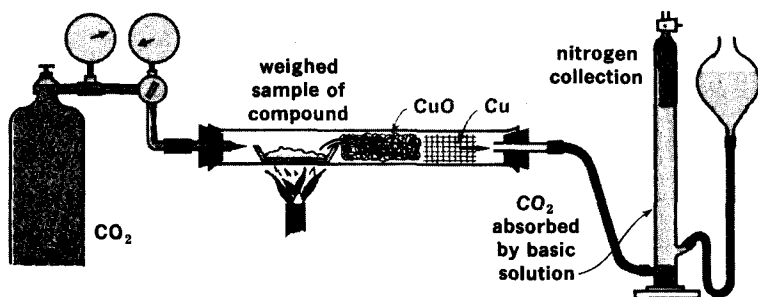


FIG. 9-2

A method for determining the percentage of nitrogen. Copper gauze is present to insure that oxides of nitrogen are reduced to  $\text{N}_2$ .  $\text{H}_2\text{O}$  and  $\text{CO}_2$  are not reduced.

dioxide gas and excess water vapor are absorbed by the  $\text{NaOH}$  solution, but the nitrogen is not. The volume of the nitrogen is measured, and, from the known density of nitrogen gas, its weight is calculated. Then:

$$\% \text{ N} = \frac{\text{weight of nitrogen}}{\text{weight of sample}} \times 100$$

Precipitation methods of analysis are frequently employed when a very slightly soluble compound can be formed. For example, if a new compound contains silver, a weighed quantity of the compound is dissolved in water, and hydrochloric acid is then added. This forms insoluble silver chloride,  $\text{AgCl}$ , which is removed by filtration, dried,

and then carefully weighed on an analytical balance. The weight of silver is  $\frac{107.9}{143.4}$  of the weight of silver chloride. Then:

$$\% \text{ Ag} = \frac{\text{weight of silver}}{\text{weight of sample}} \times 100$$

**Analytical Chemistry.** The field of chemistry that is concerned with the determination of the composition of substances is called **analytical chemistry**. The procedures described above for the determination of carbon, hydrogen, nitrogen, and silver are time-honored methods that were developed early in the history of modern chemistry. They are well adapted for research where work does not usually move at a fast tempo. In industry, however, where huge quantities of steel or aluminum or rayon or drugs or other useful substances are rolling down a production line, these methods are too slow for checking the purity of the products. Many special methods have been developed for obtaining the composition of materials in a matter of a few minutes. These methods rely on complex instruments that function on the basis of a somewhat mechanical interpretation of different wavelengths of light (color), electrical conductivity, or some other phenomenon associated with the sample being analyzed. Many colleges now give special courses in this phase of chemistry dealing with *instrumental analysis*.

## FORMULA OF NEW COMPOUNDS

**Empirical Formula.** Although the alchemist frequently employed mystical symbols to represent substances, formulas that show the actual composition of compounds were not used till about 100 years ago. In order to derive the formula for a compound, we must first determine the percentage or ratio by weight of each element in it. We can then use these data, together with the known atomic weights, to calculate the simplest ratio of ions or atoms in the compound and hence the simplest formula. As we shall see, this simplest formula, called the **empirical formula**, may or may not show the actual number of atoms in a molecule.

The following problems illustrate the calculation of empirical formulas.

**PROBLEM 12** Analysis of a certain compound of iron and chlorine reveals that 0.1396 g of iron is combined with 0.1773 g of chlorine. Calculate the empirical formula.

**Solution** These data show that the ratio by weight of iron and chlorine is 0.1396:0.1773. To obtain the ratio of moles of atoms (moles of ions in this case), each member of the weight ratio is divided by the number of grams per mole for that element:

	ratio by weight		weight per mole of atoms		ratio by moles
iron	0.1396 g	÷	55.85 g/mole	=	0.002499 mole
chlorine	0.1773 g	÷	35.45 g/mole	=	0.005001 mole

## CALCULATIONS INVOLVING FORMULAS AND EQUATIONS

Since 1 mole of atoms of any element contains the same number of atoms ( $6.02 \times 10^{23}$ ), the ratio of moles must also be the ratio of atoms.

The ratio  $\frac{\text{Fe atoms}}{\text{Cl atoms}} = \frac{0.002499}{0.005001}$  is simplified by dividing each member by

the smaller member (0.002499); this gives a ratio of  $\frac{\text{Fe atoms}}{\text{Cl atoms}} = \frac{1}{2}$  (the

slight discrepancy is attributed to experimental error in collecting the original data). This shows that there must be twice as many chlorine atoms as iron atoms to account for the ratio by weight of 0.1396 g of iron to 0.1773 g of chlorine. We conclude that the empirical formula for this compound is  $\text{FeCl}_2$ . We would need additional experimental data to interpret the formula thus:  $\text{Fe}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Cl}^-$ .

**PROBLEM 13** As a second example of calculating an empirical formula, we shall use the substance known as borax. Although this compound contains three elements, the method of calculation is the same as that followed in calculating the formula for  $\text{FeCl}_2$ . Analysis shows that borax contains 22.77 per cent sodium, Na, 21.78 per cent boron, B, and 55.45 per cent oxygen, O.

*Solution*

	ratio by weight*		weight per mole of atoms		ratio by moles
sodium	22.77 g	÷	22.99 g/mole	=	0.99 mole
boron	21.78 g	÷	10.81 g/mole	=	2.01 moles
oxygen	55.45 g	÷	16.00 g/mole	=	3.47 moles

\*It is convenient to convert the data for percentage composition into ratios by weight by taking 100 g of the substance as a basis for calculations.

The ratio of moles, 0.99:2.01:3.47, is also the ratio of atoms.

Our aim is to obtain the ratio of the atoms as small whole numbers. To simplify the ratio, we divide each member by the smallest member:

sodium	$0.99 \div 0.99 = 1.0$
boron	$2.01 \div 0.99 = 2.0$
oxygen	$3.47 \div 0.99 = 3.5$

We do not yet have the ratio in the form of whole numbers. We cannot express the formula as  $\text{NaB}_2\text{O}_{3.5}$ , because only whole numbers of atoms may appear in the formula.

By multiplying each member by 2 we convert the ratio into the smallest whole-number ratio:

sodium	$1.0 \times 2 = 2$
boron	$2.0 \times 2 = 4$
oxygen	$3.5 \times 2 = 7$

The simplest or empirical formula is  $\text{Na}_2\text{B}_4\text{O}_7$ .

**Molecular Formula.** The empirical formulas for electrovalent compounds are used to show the simplest combining ratio of ions. However, although there are no molecules as such in these compounds, the empirical formula is also called the "apparent" molecular formula.

And the weight in grams that is equal numerically to the apparent molecular weight is called 1 mole of the substance. Thus, the two formulas,  $\text{FeCl}_2$  and  $\text{Na}_2\text{B}_4\text{O}_7$ , calculated above for the salts iron(II) chloride and sodium borate, represent these substances properly. A mole of the former would weigh 126.75 g; of the latter, 201.22 g.

For a covalent compound, the formula usually shows the actual number of atoms comprising a single molecule. Often the simplest ratio of atoms corresponds to the actual number of atoms in the covalent molecule, and the empirical formula and the molecular formula are identical. Some examples that illustrate this are carbon dioxide,  $\text{CO}_2$ ; ammonia,  $\text{NH}_3$ ; and hydrogen chloride,  $\text{HCl}$ . However, in a great number of cases, the molecular formula is a multiple of the empirical formula. For example, the empirical formula for benzene is  $\text{CH}$ , but the molecular formula is  $\text{C}_6\text{H}_6$ ; the empirical formula for acetylene is also  $\text{CH}$ , but the molecular formula is  $\text{C}_2\text{H}_2$ ; and, whereas the empirical formula for glucose is  $\text{CH}_2\text{O}$ , the molecular formula is  $\text{C}_6\text{H}_{12}\text{O}_6$ .

In order to determine the molecular formula of a new covalent compound, we must experimentally determine both its molecular weight and its composition by weight. The following problem illustrates how these data are used to calculate a molecular formula.

**PROBLEM 14** Compound X was found by analysis to be 85.69 per cent carbon and 14.31 per cent hydrogen by weight. At  $27^\circ\text{C}$  and 700 mm, 300.0 ml of gaseous X weighed 0.6277 g. Calculate the molecular formula of X.

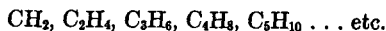
*Solution* Step 1. Calculation of empirical formula:

carbon	$85.69 \text{ g} \div 12.01 \text{ g/mole} = 7.13 \text{ moles of atoms}$
hydrogen	$14.31 \text{ g} \div 1.008 \text{ g/mole} = 14.20 \text{ moles of atoms}$

The ratio of C atoms to H atoms,  $\frac{7.13}{14.20}$ , is simplified as before to  $\frac{1}{2}$ . Hence,

the empirical formula is  $\text{CH}_2$ .

We conclude that, as far as the weight relationship is concerned, the molecular formula for X can be any in which the atoms are in a 1:2 ratio:



Step 2. Calculation of molecular weight (see Chap. 8):

	$m$	$V$	$T$	$P$
	0.6277 g	300 ml	$300^\circ\text{K}$	700 mm
	$m_2$	22,400 ml	$273^\circ\text{K}$	760 mm
$m_2 =$	$0.6277 \text{ g} \times$	$\frac{22,400 \text{ ml}}{300 \text{ ml}} \times$	$\frac{300^\circ\text{K}}{273^\circ\text{K}} \times$	$\frac{760 \text{ mm}}{700 \text{ mm}}$
	$= 55.9 \text{ g, the weight of 1 mole of X}$			

Therefore, mol. wt = 55.9 awu.

Step 3. We must now choose a formula that fits the ratio of atoms as calculated in step 1 and the molecular weight as calculated in step 2. All



## CALCULATIONS INVOLVING FORMULAS AND EQUATIONS

the formulas below in the column to the left fit the 1:2 ratio of carbon to hydrogen, but only one formula has a calculated molecular weight that agrees with the experimentally determined molecular weight:

formula	calculated mol. wt = sum of atomic weights
$\text{CH}_2$	14.027 awu
$\text{C}_2\text{H}_4$	28.054 awu
$\text{C}_3\text{H}_6$	42.081 awu
$\text{C}_4\text{H}_8$	56.108 awu
$\text{C}_5\text{H}_{10}$	70.135 awu

Molecules of X in which 4 carbon atoms are combined with 8 hydrogen atoms have the proper proportion of carbon and hydrogen by weight (85.71 per cent to 14.29 per cent) and weigh 56.108 awu. Hence, the molecular formula for X is  $\text{C}_4\text{H}_8$ . (The name of this compound is butene.)

Alternate Step 3. Finding the correct formula by writing a series of possible formulas and calculating the molecular weight of each is a trial-and-error method. A more direct approach to the problem follows.

The molecular weight is a simple multiple of the empirical formula weight,  $\text{CH}_2$ , that is, 14.027 awu.

The experimental molecular weight is 55.9 awu. Therefore,

$$\frac{55.9 \text{ awu per molecule}}{14.027 \text{ awu per empirical formula}} = 4 \text{ empirical formulas per molecule}$$

The molecular formula is  $4 \times (\text{CH}_2)$  or  $\text{C}_4\text{H}_8$ .

**PRECISE MOLECULAR WEIGHTS.** Because Avogadro's law holds only for ideal gases, the experimental method for determining molecular weights that is based on it gives approximate values only. However, we have just seen in the case of butene that only the approximate (experimental) molecular weight is necessary in obtaining the true formula.

Once the formula of a compound is obtained, its precise molecular weight can be calculated by adding the weights of the atoms that are combined in the molecule. The molecular weight thus calculated is correct to the same degree that the atomic weights are correct. In the case of butene, after we have obtained the molecular formula, we abandon the experimentally determined molecular weight in favor of the precise molecular weight, 56.108 awu, calculated by adding the weight of 4 carbon atoms ( $4 \times 12.011 \text{ awu}$ ) and 8 hydrogen atoms ( $8 \times 1.008$ ).

## GAS DENSITIES

The density of a gas is usually expressed as grams per liter at STP instead of grams per milliliter. Gas densities can be experimentally determined by carefully weighing a known volume of gas at  $0^\circ$  and 760 mm and then calculating the weight of 1 liter.

We can also calculate the ideal density of a gas from its molecular

formula. This is done by dividing the mole weight by 22.414 to obtain the weight of 1 liter. The following tabulation compares calculated ideal densities with those determined experimentally. These comparisons indicate the preciseness of Avogadro's law.

substance	formula	molar weight, g	densities, g/liter	
			calculated	determined
nitrogen	N <sub>2</sub>	28.014	1.2498	1.2506
hydrogen	H <sub>2</sub>	2.016	0.08994	0.08987
carbon dioxide	CO <sub>2</sub>	44.010	1.9635	1.9769
helium	He	4.003	0.1786	0.1785

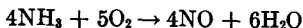
## CHAPTER REVIEW

### Terms

Percentage composition of compounds, weight relationships in chemical reactions, theoretical and actual yields, weight-volume relationships, Gay-Lussac's law of combining volumes, equivalent weight, combining weight, deduction of formulas from experimental data, experimental determination of composition of compounds, analytical chemistry, instrumental analysis, empirical formula, molecular formula, precise molecular weight, calculation of gas densities.

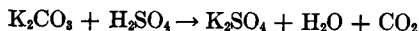
### Exercises

- Calculate the percentage by weight of each element in:
  - Sodium chloride
  - Glycerol, C<sub>3</sub>H<sub>8</sub>(OH)<sub>3</sub>
  - Xenon trichloride
  - Ammonium phosphate, (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>
- A compound of carbon and sulfur, on combustion, yielded a gas in which the partial pressure of CO<sub>2</sub> was one-half of that of SO<sub>2</sub>. Calculate the percentage of carbon in the compound.
- What is the weight of 1 mole of aluminum chloride, AlCl<sub>3</sub>; of 1 mole of Al<sup>3+</sup>; of 1 mole of Cl<sup>-</sup>?
- How many moles of oxygen are needed to oxidize 1 mole of ammonia to nitric oxide and water?



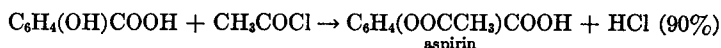
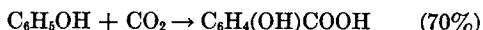
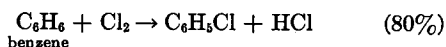
What are the weights of the ammonia and of the oxygen?

- Refer to Exercise 4. How many pound-moles of oxygen are needed to oxidize 1 pound-mole of ammonia? What are the weights of the oxygen and the ammonia?
- Calculate the weight of potassium carbonate needed to prepare 10 g of potassium sulfate according to the reaction



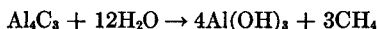
# CALCULATIONS INVOLVING FORMULAS AND EQUATIONS

7. What weight of oxygen is needed to prepare 100 g of ozone?
8. A stream of pure oxygen is passed through an ozonizer such as that shown in Fig. 6-14. The pressure of the emerging gas is 760 mm and partial pressure of the ozone is 190 mm. What is the percentage yield by weight of ozone?
9. One gram of magnesium is placed in a flask containing one gram of nitrogen, and the flask is heated. If we assume that the reaction goes to completion, what is the weight of magnesium nitride formed? Identify the reactant present in excess, and state how much of it remains at the end of the reaction.
10. A mixture of potassium chlorate and manganese dioxide, weighing 2.00 g, was heated at about 350°C in the air till the reaction was complete. After cooling the mixture was found to weigh 1.60 g. What was the weight of manganese dioxide in the sample?
11. A synthesis of aspirin from benzene is outlined below:

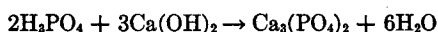


Starting with 1 ton of benzene, calculate the weight of aspirin obtained. The percentage yield of each step is indicated after the equation for that step.

12. Calculate the volume of oxygen, measured at STP, needed to oxidize 3 moles of carbon monoxide. What volume of carbon dioxide is formed?
13. What volume of oxygen, measured at 27°C and 2.00 atm, is obtained from 300 mg of sodium peroxide,  $2\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{NaOH} + \text{O}_2$ , if the recovery is 90 per cent of the theoretical?
14. Calculate the weight of zinc needed to prepare 2.0 liters of hydrogen, measured at 10 atm and 200°K:  $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$ .
15. What weight of aluminum carbide,  $\text{Al}_4\text{C}_3$ , is needed to produce 2.0 liters of methane,  $\text{CH}_4$ ?



16. A mixture of lithium and magnesium weighing 3.0 g, on burning, gave a mixture of  $\text{Li}_2\text{O}$  and  $\text{MgO}$  weighing 6.0 g. Calculate the weight of magnesium in the original sample.
17. With respect to the following reactions:



what is the equivalent weight of each: Fe,  $\text{HNO}_3$  (as the oxidizing agent),  $\text{H}_3\text{PO}_4$ ,  $\text{Ca}(\text{OH})_2$ ?

18. What weight of potassium dichromate,  $K_2Cr_2O_7$ , is needed to oxidize 100 g of hydrogen bromide,  $HBr$ , to elemental bromine? In this oxidation, the chromium changes to an oxidation state of +3.
19. What weight of hydrogen phosphate,  $H_3PO_4$ , is needed to neutralize the same amount of base that one equivalent of hydrogen sulfate,  $H_2SO_4$ , neutralizes?
20. Given the following empirical formulas and molecular weights, calculate the molecular formulas:

empirical formula	molecular weight, $\pm 3$ per cent
$CH_3$	31
$CH_2$	71
$HO$	34
$CH_2O$	88

21. A 0.2000-g sample of a new compound was decomposed in apparatus similar to that shown in Fig. 9-2. The nitrogen, collected over potassium hydroxide at  $27^\circ C$  and 760 mm, measured 20.0 ml. Calculate the percentage of nitrogen in the compound. (The  $KOH$  solution had a water vapor pressure of 20 mm at  $27^\circ C$ .)
22. A 1.000-g sample of a mineral was dissolved in concentrated nitric acid. The solution was then diluted with water to a volume of 400.0 ml. The addition of hydrochloric acid to a 50.00-ml portion of this solution gave a precipitate of  $AgCl$  that weighed 0.0081 g. Calculate the percentage of silver in the mineral.
23. A 1.800-g sample of an organic compound, containing C, H, and O, was burned in apparatus similar to that shown in Fig. 9-1. The increases in weight of the  $CO_2$  and  $H_2O$  absorbers were 2.640 g and 1.081 g, respectively. Calculate the empirical formula of the organic compound.
24. A compound was found to have the composition by weight as follows: C, 66.70 per cent; H, 7.41 per cent; N, 25.90 per cent. A molecular weight determination gave a value of  $106 \text{ awu} \pm 3$  per cent. Calculate (a) the empirical formula, (b) the molecular formula, and (c) the precise molecular weight.
25. Calculate the equivalent weight of each of the following:
  - a.  $Ba(OH)_2$  as a base
  - b.  $HClO_3$  as an acid
  - c.  $HClO_3$  as an oxidizing agent when the chlorine changes to an oxidation state of -1
  - d.  $Sr$  as a reducing agent
  - e.  $NaHSO_3$  as a reducing agent when sulfur changes to an oxidation state of +6
26. An organic compound was found by analysis to contain 5.02 per cent sulfur. This compound is also known to contain carbon, hydrogen, oxygen, and nitrogen. If we assume that one molecule of this compound contains one sulfur atom, what is its molecular weight?
27. A certain oxide of carbon is 33.3 per cent carbon by weight. Calculate the empirical formula.

## CALCULATIONS INVOLVING FORMULAS AND EQUATIONS

28. One liter of methane,  $\text{CH}_4$ , measured at  $800^\circ\text{C}$  and 2 atm is burned. What volume of oxygen, measured at the same temperature and pressure, is required for the combustion? What is the total volume of the carbon dioxide and water formed from the combustion, measured at the same  $T$  and  $P$ ?
29. A 2.000-g sample of copper chloride, on analysis, gave 0.945 g of copper and 1.055 g of chlorine. Calculate the empirical formula.
30. A 1.00-g sample of the hydrate  $\text{CoSO}_4 \cdot x\text{H}_2\text{O}$  gave, on heating, 0.55 g of the anhydrous salt, cobalt(II) sulfate. What is the formula of the hydrate?
31. Why do we write  $\text{CO}_2$  instead of  $\text{C}_2\text{O}_4$  for the gas carbon dioxide? Why do we write  $\text{C}_2\text{H}_4$  for the gas ethene instead of  $\text{CH}_2$ ?
32. Calculate the densities of the following gases from their formulas: ethane,  $\text{C}_2\text{H}_6$ ; argon, Ar; chloroform,  $\text{CHCl}_3$ , at  $100^\circ\text{C}$ ; carbon monoxide, CO, at  $200^\circ\text{K}$  and 3 atm.
33. A mixture of  $\text{N}_2$  and  $\text{H}_2$  has a volume of 5.0 liters at  $27^\circ\text{C}$  and 5.0 atm. The  $\text{H}_2$  partial pressure in the mixture is 2.0 atm. When this mixture is passed over a catalyst at  $200^\circ\text{C}$ , 10 per cent of the theoretical yield of  $\text{NH}_3$  (ammonia) is formed. Calculate the weight of the ammonia formed.
34. The following is quoted from William Whewell's *Philosophy of the Inductive Sciences*, 1840:

The proportions of potassa and soda which [react with acid to] form neutral salts are 590 and 391 in one case, and therefore in all. . . . 590 of potassa is *equivalent* to 391 of soda. . . . We find that potassa is a compound of a metallic base, potassium, and of oxygen, in the proportion of 490 to 100; we suppose, then, that the particle of potassa consists of a particle of potassium and a particle of oxygen . . . we may call *atoms*, and assume to be indivisible.

  - a. Using our present symbols for the elements, what formulas would Whewell assign to potassa and soda?
  - b. Using 100 as the atomic weight of oxygen, what atomic weights would Whewell assign to potassium and sodium?
  - c. Using 16 as the atomic weight of oxygen, what atomic weights would Whewell assign to potassium and sodium?
  - d. Based on modern atomic weights and the old combining proportions, what formulas and names would we give "potassa" and "soda" today?
  - e. In addition to atomic weight differences, what other concept is obviously different as shown by our formulas in contrast to those written in part a.?

## SUPPLEMENTARY READING

- Kieffer, W. F.: *The Mole Concept in Chemistry*, Reinhold Publishing Corporation, New York, 1962.
- Trousdale, E. A.: "Solution of Problems in Chemistry," *J. Chem. Educ.*, 35: 299 (1958).

## SOLUTIONS



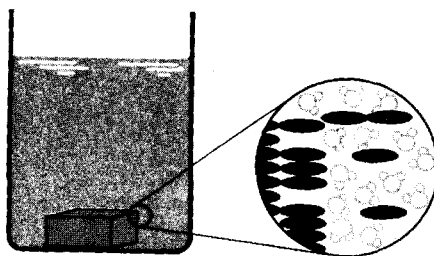
Solutions play an important part in

many processes that go on about us. Nutrients are carried in water solution to all parts of a plant; the body fluids of animals are water solutions of numerous substances. The ocean is a vast water solution containing different compounds extracted from the minerals of the earth's crust. Medicines and drugs are frequently aqueous or alcoholic solutions of physiologically active compounds. The production of many useful materials by the chemical industry involves chemical reactions in which the reacting substances are dissolved in water, alcohol, ether, benzene, or other solvents.

### NATURE OF SOLUTIONS

A **solution** is a homogeneous mixture of the molecules, atoms, or ions of two or more different substances. Because a solution is a mixture, its composition is variable. Solutions differ from other types of mixtures in that only one phase is present; that is, no part is separated from another by a detectable boundary. The mixture is *homogeneous*. In *heterogeneous* mixtures, definite surfaces can be detected, showing there are separate parts of the mixture. Muddy water is an example of a heterogeneous mixture consisting of two phases, the small particles of clay and the water. The clay particles are not single molecules but are composed of many particles clustered together. The larger clusters can be seen with a microscope; in time, they settle to the bottom, or they may be removed by filtration.

The nature of a solution may be better understood by picturing what is thought to happen when a lump of sugar is dissolved in water. In this process sugar molecules break away from the lump of sugar and



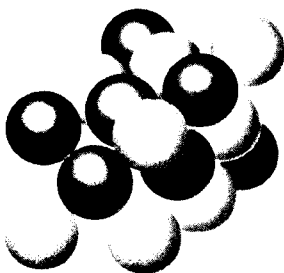
As sugar dissolves in water, its molecules become scattered among the water molecules.

FIG. 10-1

become dispersed in the water (Fig. 10-1). The sugar particles are too small to reflect light, so that they cannot be seen even with the most powerful microscope. If this solution is poured through a filter paper, the sugar molecules pass through the pores of the paper along with the water molecules. Further, the sugar particles diffuse into all parts of the solution. Therefore, the composition of any part of the solution becomes identical with that of any other part.

When common salt,  $\text{NaCl}$ , is dissolved in water, again we have small particles ( $\text{Na}^+$  ions and  $\text{Cl}^-$  ions) breaking away from the attractive forces that hold them in the solid form. They become uniformly mixed with molecules of water. The salt solution differs from the sugar solution in that the latter is a mixture of molecules of two different substances, whereas the former is a mixture of the ions of one substance with the molecules of a second substance.

If copper and gold are melted together, the atoms intermingle so that the molten liquid appears to be a single substance. On cooling and solidifying, the atoms do not aggregate into small lumps of copper and small lumps of gold. Instead, single atoms of copper take positions between atoms of gold (Fig. 10-2) to form a mixture called a solid solu-



Diagrammatic representation of a solid solution of copper and gold.

FIG. 10-2

tion. In this case, the solution is a mixture of the atoms of two substances. A 12-carat yellow-gold ring is a solid solution containing 50 per cent gold and 50 per cent copper by weight. (Pure gold is said to be 24 carat.)

**Solute and Solvent.** The dissolved substance in a solution is called the solute and the dissolving medium is called the solvent. In a solu-

tion of salt in water, salt is the solute and water is the solvent. These terms have little meaning when applied to certain solutions. For example, solute and solvent apply equally well to either component of a solution containing 50 per cent alcohol and 50 per cent water.

**Types of Solutions.** Because there are three states of matter, there are three types of solutions: **gaseous solutions**, **liquid solutions**, and **solid solutions**. When a solid such as sugar is dissolved in water, the sugar is no longer in the solid state; the sugar molecules are free to move about as the water molecules do. This solution is classified as a *liquid* solution. When water evaporates into a gas—for example, oxygen—the solution formed is a *gaseous* solution. The water molecules are widely separated from other molecules and behave generally as other gaseous molecules do.

Solutions may be subclassified from the standpoint of the final state of the solution and the normal state of the pure solute. Nine combinations are possible (three for each final state):

1. The solution is a liquid.
  - a. The *solute* was a *solid*. Sugar dissolved in water.
  - b. The *solute* was a *liquid*. Alcohol dissolved in water; lubricating oil dissolved in gasoline.
  - c. The *solute* was a *gas*. Oxygen dissolved in water; carbon dioxide dissolved in water.
2. The solution is a solid.
  - a. The *solute* was a *solid*. Brass (copper and zinc); yellow gold (copper and gold).
  - b. The *solute* was a *liquid*. Mercury dissolved in silver. (This solution is an amalgam and is used in filling teeth.)
  - c. The *solute* was a *gas*. This type of solution is rare. Hydrogen dissolved in metallic palladium is perhaps the best-known example. There appear to be "holes" in the crystal structure of palladium large enough for single atoms of hydrogen to enter. The number of these "holes" is equal to about one-half of the number of palladium atoms present.
3. The solution is a gas.
  - a. The *solute* was a *solid*. The evaporation of such solids as camphor and naphthalene into the air produces a mixture in which the molecules of a solid are scattered in a gas.
  - b. The *solute* was a *liquid*. When water, alcohol, ether, etc., evaporate into the air at room temperature, the molecules of these liquids are scattered among molecules of gases.
  - c. The *solute* was a *gas*. Any mixture of two or more gases can be called a solution, because the particles of any gaseous substance are the individual molecules.

Whether the gaseous type of solution is properly called a solution is a debatable question. Van der Waals and electrostatic forces be-



tween solute and solvent molecules have hardly any effect in the formation of a solution in the gaseous state, because the particles are so widely separated.

### WHY SUBSTANCES DISSOLVE

Although it is beyond the scope of this book to mention all factors involved in the formation of a solution, the ones of prime importance in forming liquid solutions are (1) interaction of solute and solvent to form solvated particles, (2) reaction of solute and solvent to form a new substance that becomes solvated, and (3) the tendency of systems to attain a maximum disorder.

*Solvation.* *Solvation* is the interaction of solvent molecules with solute molecules or ions to form aggregates whose particles are loosely bonded together. When water is used as the solvent, the process is also called *aquation* or *hydration*.

We saw in Chap. 5 that many covalent compounds are composed of polar molecules. Water is a familiar example. When a small crystal of an ionic substance such as sodium chloride is placed in water, the polar molecules orient themselves about the face of the crystal, as shown in Fig. 10-3. The attractive force between the water molecules

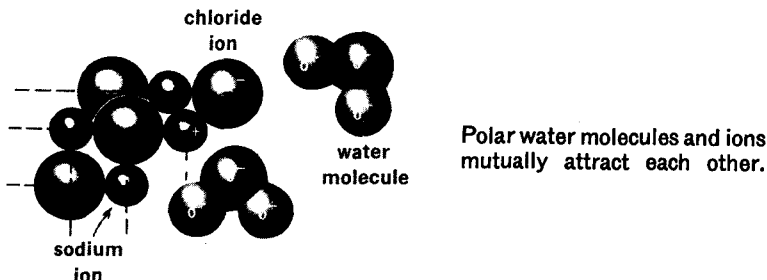
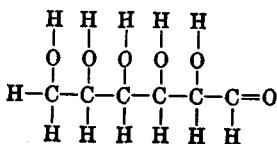


FIG. 10-3

and the surface ions is great enough to cause the ions to leave their fixed positions in the crystal and to move to positions between the water molecules. Water molecules are actually loosely bonded to a sodium ion or a chloride ion in solution, as shown in Fig. 10-4. Both ions are said to be solvated or aquated.

Solvation is not limited to ionic compounds. Any polar covalent solute may interact with a polar solvent. Glucose sugar is a



covalent compound with polar groups that dissolves in water because of solvation. Each hydroxyl group ( $-\text{O}-\text{H}$ ) represents a

Solvation of  $\text{Na}^+$  and  $\text{Cl}^-$  ions. The number of water molecules held by these simple ions is indefinite.

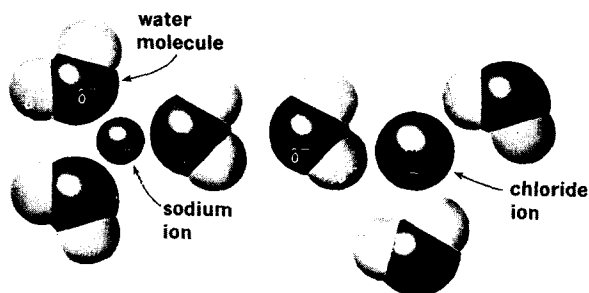
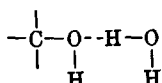
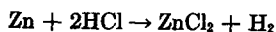


FIG. 10-4

region in which the oxygen is relatively negative and the hydrogen is relatively positive. When a small crystal of sugar is placed in water, water molecules tend to orient themselves about a surface sugar molecule so that the positive or negative parts of the water molecules are directed toward the oppositely charged parts of the sugar molecule. The sugar molecule leaves the surface of the crystal and goes into solution as an aquated molecule. In this case we may say that the water molecules are bonded to the sugar molecule by hydrogen bonds:



**Chemical Reaction Followed by Solvation.** When a small piece of zinc is added to water that contains some  $\text{HCl}$ , the zinc appears to dissolve. The same is true of a piece of marble ( $\text{CaCO}_3$ ). In these cases, the zinc and marble have been chemically changed, because on careful evaporation of the solutions, zinc and marble are not obtained. Zinc and marble do not dissolve as such; rather, chemical reactions occur that produce ionic compounds:



The ions of the compounds then become aquated in the same manner as described for  $\text{NaCl}$ .

**DIELECTRIC CONSTANT.** In addition to the attraction between solute and solvent molecules, there is another important phenomenon to consider when ionic solutes dissolve. Solvents differ in their ability to reduce the attraction between positive and negative solute ions. If two such ions of opposite charge exist in a vacuum, there is a certain force of attraction  $F$  between them at a given distance. But if another substance—for example, a solvent—is in the space separating these ions, their attraction for each other is less. The fraction  $1/D$  by which

the attractive forces between separated charges is decreased by a substance is determined by the dielectric constant  $D$  of that substance.

Water has a high dielectric constant, about 80. Ions that are widely separated in water attract one another with only  $1/80 F$ . In general, polar liquids have high dielectric constants (Table 10-1).

TABLE 10-1 *Dielectric constants*

solvent	dielectric constant	solvent	dielectric constant
hydrogen sulfate, $H_2SO_4$	84 (20°C)	liquid ammonia, $NH_3$	22 ( $-33^\circ C$ )
water, $H_2O$	80 (20°C)	ether, $(C_2H_5)_2O$	4.3 (20°C)
methyl alcohol, $CH_3OH$	33 (20°C)	benzene	2.3 (25°C)
ethyl alcohol, $CH_3CH_2OH$	24 (25°C)	vacuum	1 (by definition)

**Maximum Disorder.** Consider a bulb of helium connected to a bulb of methane ( $CH_4$ ), as shown in Fig. 10-5. When the stopcock is opened, the two gases diffuse in both directions, so that a homogeneous mixture (solution) results. The reverse has never been observed; that is, if we start with a uniform mixture of helium and methane in the two bulbs, diffusion does not occur so that all the methane accumulates in one bulb and helium in the other. We may say that the system

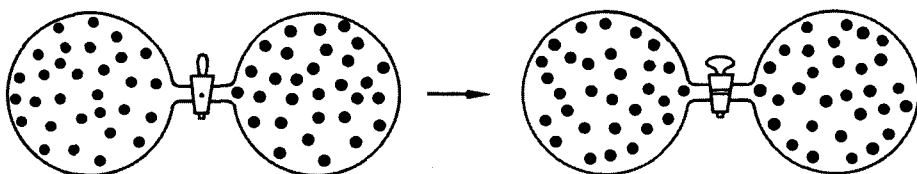


FIG. 10-5 Schematic illustration of the tendency to attain maximum entropy (maximum disorder).

does not spontaneously achieve maximum order. This experiment illustrates an important principle that is discussed in considerable detail in Chap. 16 under the heading of **entropy**. Physical and chemical systems tend to seek a state of maximum disorder (maximum entropy).

The tendency for systems to attain maximum disorder is observed when substances other than gases are brought together. For example, hexane ( $C_6H_{14}$ ) and heptane ( $C_7H_{16}$ ), two liquid hydrocarbons, mix in all proportions to form a solution. Because the attraction of molecules of hexane for one another, of molecules of heptane for one another, and of molecules of hexane for molecules of heptane are about the same, the formation of the solution may be attributed largely to the tendency to achieve maximum disorder (maximum entropy).

It is important to note that the effect on the solution process of the

entropy change is often quite small in comparison with solvation or other effects. Indeed, the strong forces that exist between solute and solvent particles may result in the formation of a solution even when the entropy of the system decreases. Conversely, the strong attractive forces among ions or polar molecules may prevent ionic or polar compounds from scattering to any extent in a nonpolar solvent, or the strong attractive forces among polar solvent molecules may prevent nonpolar compounds from dissolving appreciably, even though the formation of a solution would result in an increase in entropy.

**GENERALIZATION.** There is a strong tendency for ionic or polar covalent compounds to dissolve in polar solvents and for nonpolar compounds to dissolve in nonpolar solvents. In other words, like dissolves like.

**Insoluble Substances.** If a substance is very slightly soluble, say less than 0.1 g of solute in 1,000 g of solvent, the chemist may call it insoluble. Probably nothing is absolutely insoluble in a given solvent, but many things are practically insoluble, for example, glass in water.

When two liquids are mutually insoluble, they are said to be **immiscible** (Fig. 10-6). Such liquids—oil and water, for example—separate into layers. Study of immiscible liquid systems has shed light on problems of likeness and unlikeness of molecular structure.

A system of three immiscible liquids.

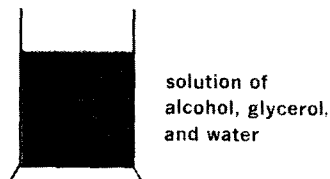
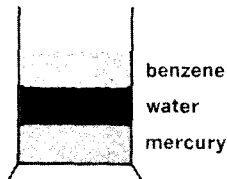


FIG. 10-6

## SATURATED, UNSATURATED, AND SUPERSATURATED SOLUTIONS

When a lump of sugar is placed in water, molecules break away from the surface of the sugar and pass into the solvent, where they move about in the same manner as the water molecules. Because of this random motion, some of them collide with the surface of the sugar and are held there by the attractive forces of the other sugar molecules. It can be shown that the sugar is dissolving and crystallizing at the same time. When the sugar is first placed in the water, the rate of dissolving is very rapid as compared with the rate of crystallizing. As time goes on, the concentration of the dissolved sugar steadily increases, and the rate of crystallizing increases. When the rates of crystallizing and dissolving become the same, the process is said to be *at equilibrium* and the solution is said to be **saturated**. If the excess sugar is left in contact with the solution, this process of dissolv-

ing and crystallizing continues at equilibrium, but the concentration of the solution does not change, because the two processes are proceeding at the same rate. A **saturated solution** is defined as one that contains the amount of dissolved solute necessary for the existence of an equilibrium between dissolved and undissolved solute. The formation of a saturated solution is hastened by vigorous stirring and an excess of solute.

An **unsaturated solution** is one that is less concentrated (more dilute) than a saturated solution, and a **supersaturated solution** is one that is more concentrated than a saturated solution. Note that a saturated solution is not necessarily a concentrated solution. For example, when limestone rock (calcium carbonate,  $\text{CaCO}_3$ ) remains in contact with a quantity of water till an equilibrium is reached between dissolved and undissolved calcium carbonate, the saturated solution is extremely dilute, because calcium carbonate is not very soluble.

**Preparation of Supersaturated Solutions.** A supersaturated solution is usually prepared by first making a saturated solution at an elevated temperature. A solute is used that is much more soluble in the warm than in the cool solvent. Any undissolved solute is removed by filtering the hot solution, after which the solution is cooled carefully so as to avoid crystallization. This means that the solution must not be jarred or shaken, and that dust and other foreign matter must be excluded. If no solute separates during cooling, the cool solution is supersaturated. A supersaturated solution is an *unstable system*. It may be converted to a saturated solution by adding a small "seed" crystal (usually of the solute, although often a foreign substance works just as well). This crystal provides a nucleus about which the excess dissolved solute can crystallize (Fig. 10-7). Sodium acetate and sodium thiosulfate (hypo) readily form supersaturated solutions when treated in this way.



Left: A supersaturated solution of sodium acetate about to be "seeded." Center: Crystallization of some sodium acetate about 30 sec later. Right: Completion of the process about 2 min later. The solution is now saturated.

FIG. 10-7

One of the most interesting of nature's supersaturated solutions is air supersaturated with water vapor. One way in which this unstable system can be broken is by the addition of seed crystals of silver iodide,  $\text{AgI}$ .

Solubilities of certain solids  
at different temperatures.

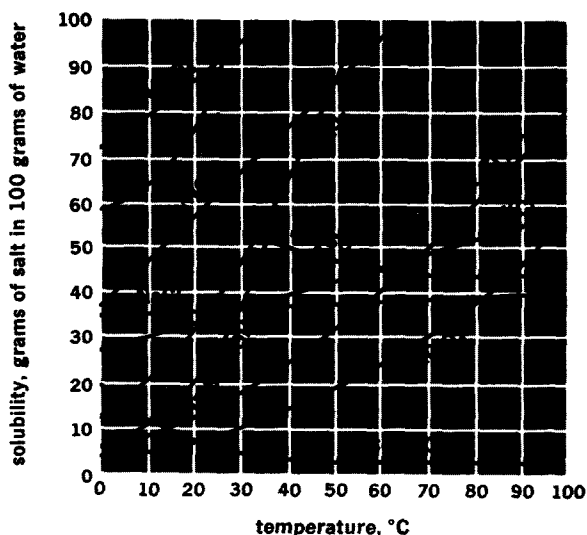


FIG. 10-8

## FACTORS THAT INFLUENCE SOLUBILITY

The amount of solute that dissolves in a given amount of solvent to produce a saturated solution is called the **solubility** of that solute. If large amounts dissolve, the substance is said to be very soluble; if only small amounts dissolve, the substance is described as being slightly or moderately soluble; if an extremely small quantity dissolves, the substance is said to be insoluble. Three factors determine solubility: the nature of the solute and solvent, temperature, and pressure. We have already considered the effect of the nature of the solute and solvent on solubility, so that we need consider only the effect of temperature and pressure here.

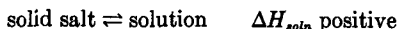
**Effect of Temperature. SOLIDS IN LIQUIDS.** Most solids become more soluble in a liquid as the temperature rises. There are a few solids that become less soluble as the temperature increases. In Fig. 10-8 the solubilities of several compounds in grams per 100 g of water are plotted against temperature. It will be noticed that, with the exception of sodium sulfate and cerium sulfate, the solubilities increase as the temperature rises; for example, the solubility of potassium nitrate,  $\text{KNO}_3$ , at  $0^\circ\text{C}$  is 13 g per 100 g of water, and at  $50^\circ$  it is 86 g. At about  $35^\circ\text{C}$ , the solubility of hydrated sodium sulfate begins to decrease as the temperature rises, because of the decomposition of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  to form  $\text{Na}_2\text{SO}_4$ .

In seeking an explanation of why some solids become more soluble as the temperature rises and others become less, let us consider the

heats of solution. We frequently observe that, when substances dissolve, the newly made solution is warm to the touch in some cases and cool in others. For example, when sodium hydroxide is dissolved in water, heat energy is liberated to the surroundings and the temperature rises; the reverse is true when solid ammonium chloride is dissolved in water. These heat effects are due to the making and breaking of ionic and covalent bonds by the solution process.

The heat of solution or enthalpy change,  $\Delta H_{\text{soln}}$ , may vary considerably, depending on whether solute *A* is added to pure solvent, or to a dilute solution of *A*, or to a concentrated solution of *A*, etc. Because we are concerned here with saturated solutions, the heat effects under discussion are those produced when a small amount of solute *A* dissolves in, or crystallizes from, a saturated solution of *A*.

Consider a saturated solution of either NaCl or  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  at some temperature, say 20°. The following equilibrium exists between the undissolved salt and the solution:



Heat is absorbed as the salt goes into solution and evolved as the salt crystallizes. Because both processes are going on at the same rate, the net energy change is zero. However, when heat energy is added from an outside source, as is done to raise the temperature, the process absorbing heat is favored. The solution process, which absorbs heat, begins to take place more rapidly than the crystallization process; more NaCl or  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  dissolves. For a substance with a negative  $\Delta H$  of solution (the solution process liberates heat), the crystallization process is favored when the temperature rises.

As we can see in Fig. 10-8, sodium sulfate is an example of intriguing behavior. Below 32.4°C the hydrated salt is the stable solid form; above this temperature the anhydrous salt is the stable solid form. Because the former dissolves with the absorption of heat (below 32.4°C) and the latter with the evolution of heat (above 32.4°), the solubility of sodium sulfate in water increases as the temperature rises till 32.4°C is reached, and then the solubility decreases as the temperature continues to rise.

Our interpretation of the effect of temperature changes on solubility is based on Le Chatelier's principle, stated by the French chemist Henry Louis Le Chatelier (1850–1936): *When a stress is brought to bear on a system at equilibrium, the system tends to change so as to relieve the stress.* The stress being brought to bear in the case under discussion is the addition or removal of heat energy (temperature change). In the saturated solution (equilibrium solution) discussed previously, when heat is added, the process that tends to take up the added heat is favored. A substance that absorbs heat when dissolving in a saturated solution tends to be more soluble at a higher temperature; and one that liberates heat tends to be more soluble at a lower temperature.

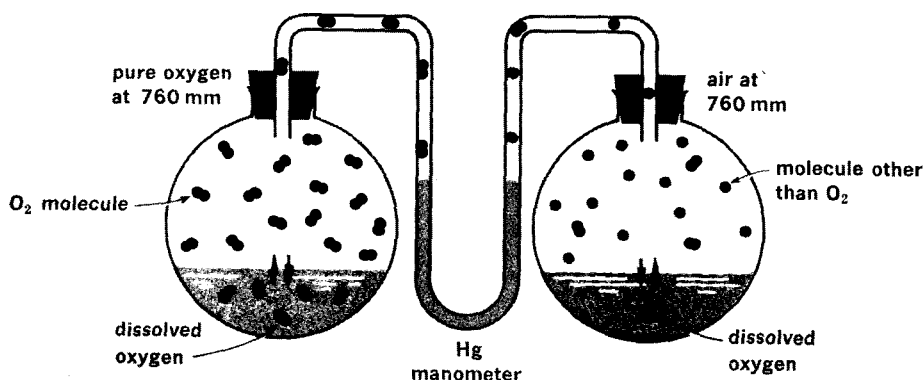


FIG. 10-9

A diagrammatic representation of Henry's law. Note that the partial pressure of oxygen in the flask on the left is about five times that on the right. Hence, about five times as much dissolved oxygen is indicated in the flask on the left.

**GASES IN LIQUIDS.** The solubility of a gas in a liquid usually decreases as the temperature increases. Because of this, carbon dioxide bubbles vigorously out of a carbonated drink if the liquid is warmed. For the same reason, when tap water is heated, bubbles of air begin to appear when the water is lukewarm.

**Effect of Pressure.** Pressure changes have little effect on solubility if the solute is a liquid or a solid. However, in the formation of a saturated solution of a gas in a liquid, the pressure of the gas plays an important part in determining how much of the gas dissolves. *The weight of a gas dissolved by a given amount of a liquid is directly proportional to the pressure exerted by the gas when in equilibrium with the solution.* This is a statement of Henry's law. Figure 10-9 is a graphic illustration of this law. Henry's law does not hold well for gases that react with the solvent, for example, hydrogen chloride or ammonia dissolved in water.

## EXPRESSING CONCENTRATIONS

The concentration of a solution refers to the weight or volume of the solute present in a specified amount of the solvent or solution. There are several common methods of expressing these amounts.

**Per Cent by Weight.** When expressing per cent by weight, the percentage given refers to the solute; for example, a 5 per cent aqueous NaCl solution contains 5 per cent by weight of sodium chloride, the remaining 95 per cent being water.

**Per Cent by Volume.** The concentration of a solution of two liquids is frequently expressed as a volume percentage, because the volumes



of liquids are easily measured. The concentration of alcoholic beverages is usually expressed this way. A wine that is 12 per cent alcohol has 12 ml of alcohol per 100 ml of wine.

**Molar Solutions.** Knowledge of the number of solute particles in a given quantity of solution is required in many laboratory operations. The usual way of expressing the number of particles present is in terms of the number of moles:

name	formula	weight of 1 mole, g	number of particles
alcohol	$C_2H_6O$	46	$6.02 \times 10^{23}$ molecules
glycerin	$C_3H_8O_3$	92	$6.02 \times 10^{23}$ molecules
sugar	$C_{12}H_{22}O_{11}$	342	$6.02 \times 10^{23}$ molecules
salt	$NaCl$	58.5	$12.04 \times 10^{23}$ $Na^+$ and $Cl^-$ ions

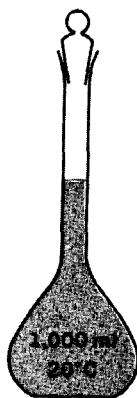


FIG. 10-10

A **one molar** (1 *M*) solution contains 1 mole of solute per liter of solution, a **two molar** (2 *M*) solution contains 2 moles per liter of solution, and so on. To make a 0.1 *M* sugar solution, we weigh a tenth of a mole (34.2 g) of sugar and place it in a volumetric flask (Fig. 10-10);

Volumetric flasks are calibrated to hold a specified volume at a specified temperature when filled to the mark on the neck.

then we add water until the flask is about three-fourths full. The mixture is then stirred until all the sugar is dissolved. Finally, we add water until the total volume is precisely 1 liter. To make a 0.1 *M* glycerin solution, the procedure is exactly the same, except that 9.2 g of glycerin is used. The liter of 0.1 *M* glycerin solution contains the same number of dissolved glycerin molecules as there are sugar molecules in the liter of 0.1 *M* sugar solution. The amount of water in the two solutions differs to a slight extent.

**PROBLEM 1** What weight of calcium bromide,  $CaBr_2$ , is needed to prepare 150 ml of a 3.5 *M* solution?

*Solution*

$$\text{wt solute} = (\text{molarity})(\text{vol in liter})(\text{wt of 1 mole})$$

$$\begin{aligned} \text{wt calcium bromide} &= \left( \frac{3.5 \text{ moles}}{\text{liter}} \right) \left( 150 \text{ ml} \times \frac{1 \text{ liter}}{1,000 \text{ ml}} \right) \left( \frac{200 \text{ g}}{\text{mole}} \right) \\ &= 105 \text{ g } CaBr_2 \end{aligned}$$

**Molal Solutions.** As just indicated, solutions of the same molarity have slightly different ratios of molecules of solute to molecules of solvent, depending on what solutes are involved. In order that he know precisely the solute-solvent ratio, the chemist may express the concentration in terms of the **molality** (*m*), the number of moles of solute dissolved per kilogram (kg) of solvent.

**Mole Fraction.** The fractional part of the total number of moles of solute and solvent due to the solute is the **mole fraction of the solute**;

the fractional part of the total due to the solvent is the **mole fraction of the solvent**.

**PROBLEM 2** Calculate the mole fractions of alcohol,  $C_2H_5OH$ , and water in a solution made by dissolving 9.2 g of alcohol in 18.0 g of water.

*Solution*

$$\text{no. of moles of } C_2H_5OH = \frac{9.2 \text{ g}}{46 \text{ g/mole}} = 0.20 \text{ mole}$$

$$\text{no. of moles of } HOH = \frac{18.0 \text{ g}}{18 \text{ g/mole}} = 1.0 \text{ mole}$$

$$\text{total number of moles} = 1.2$$

$$\text{mole fraction of } C_2H_5OH = \frac{0.20}{1.2} = 0.17$$

$$\text{mole fraction of } HOH = \frac{1.0}{1.2} = 0.83$$

One-sixth (0.17) of all the molecules in this solution are alcohol molecules. Note that the mole fractions of solute and solvent add to unity.

**Normal Solution.** The **normality** ( $N$ ) of a solution is the number of equivalent weights (see Chap. 9) of solute per liter of solution. A one normal (1  $N$ ) solution contains 1 equivalent weight per liter of solution, a 0.5  $N$  solution contains one-half equivalent weight per liter, etc.

It is especially convenient to express concentrations in terms of normalities when we are dealing with solutions which react with one another.

**PROBLEM 3** Calculate the weight of barium hydroxide,  $Ba(OH)_2$ , required to make 50 ml of a 0.10  $N$  solution.

*Solution* The weight of a mole is 171.4 g. Because there are 2  $OH^-$  ions per unit of  $Ba(OH)_2$ , this weight is divided by 2 to obtain the equivalent weight:

$$171.4 \text{ g} \div 2 = 85.7 \text{ g, equiv. wt of } Ba(OH)_2$$

$$\text{By definition, normality } (N) = \frac{\text{no. equiv. wt}}{\text{vol (in liters) of solution}}$$

Since  $\text{wt solute} = \text{no. of equiv. wt} \times \text{wt of 1 equivalent}$ , it follows that:

$$\text{wt solute} = (\text{normality}) (\text{vol in liters}) (\text{wt of 1 equivalent})$$

$$\begin{aligned} \text{wt } Ba(OH)_2 &= \left( \frac{0.10 \text{ equiv. wt}}{1 \text{ liter}} \right) \left( 50 \text{ ml} \times \frac{1 \text{ liter}}{1,000 \text{ ml}} \right) \left( \frac{85.7 \text{ g}}{\text{equiv. wt}} \right) \\ &= 0.43 \text{ g } Ba(OH)_2 \end{aligned}$$

**PROBLEM 4** Calculate the molarity of a solution made by dissolving 1.0 g of phenol,  $C_6H_5OH$ , in enough water to make 50 ml of solution.

*Solution* By definition,

$$\begin{aligned}\text{molarity } (M) &= \frac{\text{no. moles of solute}}{\text{vol (in liters) of solution}} \\ &= \frac{1.0 \text{ g phenol} \times 1 \text{ mole/94 g phenol}}{50 \text{ ml} \times 1 \text{ liter/1,000 ml}} \\ &= 0.21 \frac{\text{mole}}{\text{liter}} = 0.21 M\end{aligned}$$

**PROBLEM 5** Calculate the molality of the solution made by dissolving 1.0 g of phenol in 50 g of water.

*Solution* By definition,

$$\begin{aligned}\text{molality } (m) &= \frac{\text{no. moles of solute}}{\text{wt (in kg) of solvent}} \\ &= \frac{1.0 \text{ g phenol} \times 1 \text{ mole/94 g phenol}}{50 \text{ g H}_2\text{O} \times 1 \text{ kg/1,000 g H}_2\text{O}} \\ &= 0.21 \frac{\text{mole}}{\text{kg solvent}} = 0.21 m\end{aligned}$$

Note that the solutions in problems 4 and 5 have different concentrations, although the molarity of one is numerically the same as the molality of the other.

## TITRATION OF ACIDS AND BASES

**Titration** is the process of determining the amount of a solution of known concentration that is required to react completely with a certain amount of a sample that is being analyzed. The solution of known concentration is called a *standard solution*, and the sample being analyzed is referred to as the *unknown*.

In the analysis of acidic and basic solutions, titration involves the careful measurement of the volumes of an acid and a base that just neutralize each other. Suppose that we have a hydrochloric acid solution whose concentration we wish to determine, and that we have on hand in the laboratory a standard base solution with a concentration of 1.20 *N*. The titration is carried out as follows. Portions of the two

A titration is performed with burettes.

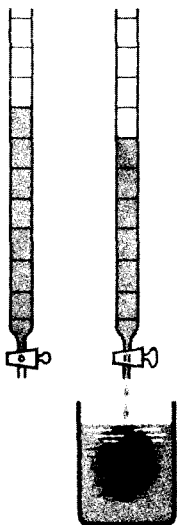


FIG. 10-11

solutions are placed in separate burettes (Fig. 10-11), and a convenient quantity of the acid, say 15.0 ml, is measured from its burette into the beaker. An indicator (litmus or phenolphthalein) is added to the acid, and the beaker is placed under the burette containing the base. The base is permitted to run into the beaker rather rapidly at first, then slowly, and finally drop by drop till a single final drop causes the indicator to change color. This color change is the signal that reveals the *end point* of the titration. At the end point an amount of base has been added that is equivalent in chemical reactivity to the amount of acid in the 15.0 ml of the unknown solution. The total volume of base used is read from the burette. Suppose that this vol-

ume is 21.2 ml. This means that 21.2 ml of a 1.20 *N* base is found to just neutralize 15.0 ml of hydrochloric acid of unknown concentration. From consideration of the experimental data:

	base	acid
volume	21.2 ml	15.0 ml
normality	1.20	?

we can see that the acid is more concentrated than the base, because a smaller volume of it was required. That is, even before we calculate it, we know that the normality of the acid is going to be greater than 1.20 *N*. The concentration of the acid is calculated by using the general relationship that states that the product of the volume times the normality is equal for all solutions that react completely with one another:

$$V_{\text{acid}} \times N_{\text{acid}} = V_{\text{base}} \times N_{\text{base}}$$

The volumes may be expressed in liters or milliliters as long as consistent units are used. With this relationship, the calculations are

$$15.0 \text{ ml} \times N_{\text{acid}} = 21.2 \text{ ml} \times 1.20 \text{ } N$$

$$N_{\text{acid}} = \frac{21.2 \text{ ml} \times 1.20 \text{ } N}{15.0 \text{ ml}} = 1.70 \text{ } N$$

The concentration of a basic solution of unknown concentration can be determined in a similar fashion. A standard acid solution is required for this titration.

Litmus, a dye extracted from a moss (*litr* = color + *mosi* = moss), was one of the first natural organic dyes to be used as an acid-base indicator. Certain vegetable colors—for example, grape juice, elderberry juice, red cabbage—contain molecules that change color, owing to structural changes accompanying the gain or loss of a proton, and can be used as indicators for crude titrations. Today many indicators are synthetic organic compounds. Phenolphthalein is an example.

## PROPERTIES OF SOLUTIONS

We are familiar with the use of water solutions of alcohol and ethylene glycol in automobile radiators during the winter. Their use depends on the fact that these solutions freeze at a lower temperature than water alone does. These are not the only substances that lower the freezing point of water. Any soluble compound such as salt, sugar, hydrochloric acid, or baking soda, when dissolved in water, forms a solution that has a lower freezing point than pure water does. Moreover, the boiling points and vapor pressures of these solutions are also different from those of the pure solvent (Fig. 10-12). To what extent do they differ? For solutions of nonvolatile nonelectrolytes, the answer to this question is provided by the following law. *The freezing point, boiling point, and vapor pressure of a solution differ from those of*

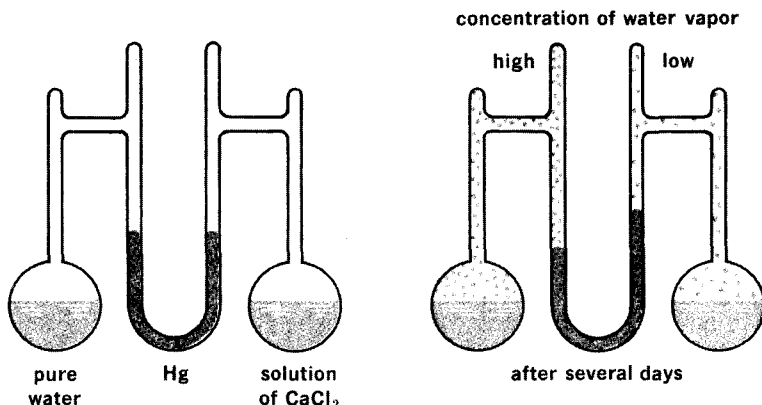


FIG. 10-12

When the bulbs are first sealed in position (left) the mercury level is the same in each limb of the U-tube. As water evaporates from both bulbs, the mercury levels slowly shift and, after a short time, the system comes to equilibrium (right). The position of the mercury levels show how much greater the water vapor pressure of the pure water is than the water vapor pressure of the solution.

*the pure solvent by amounts which are directly proportional to the molal concentration of the solute.*<sup>1</sup>

The kind of solute matters very little so long as (1) it does not have an appreciable vapor pressure and (2) it does not form ions.

The solution properties referred to above—freezing point depression, boiling point elevation, and change in vapor pressure—are referred to as **colligative properties**. Osmotic pressure is also a colligative property. Colligative properties are uniformly affected by changes in the molal concentration (changes in the number of solute molecules in a constant quantity of solvent molecules) but not by the specific nature of the solute. (In a 1 molal solution there is 1 mole of solute per 1 kg of solvent.)

## FREEZING POINT OF SOLUTIONS

If some sugar is dissolved in water and the solution is then cooled, ice crystals do not form at a temperature of 0°C, but at some lower temperature. At what temperature do ice crystals begin to form in a water solution? According to the colligative property law, the amount by which the freezing point is lowered is determined by the number, not the kind, of dissolved molecules in a given amount of solvent.<sup>2</sup> It has been determined experimentally that 1 mole ( $6.02 \times 10^{23}$  molecules) of any nonelectrolyte dissolved in 1 kg (1,000 g) of water

<sup>1</sup> For convenience we shall refer to this law as the colligative property law. As it applies to the vapor pressure, this statement is known as Raoult's law (1887).

<sup>2</sup> In the case of the freezing-point change, the colligative property law applies not only to nonvolatile but also to volatile solutes, for example, methyl alcohol (wood alcohol) and ethyl alcohol (grain alcohol).

lowers the freezing point by  $1.86^{\circ}\text{C}$ ; that is, ice crystals begin to form when the temperature is lowered to  $-1.86^{\circ}\text{C}$ . On the other hand, if 0.5 mole ( $3.01 \times 10^{23}$  molecules) is dissolved in 1,000 g of water, the amount by which the freezing point is lowered is  $0.93^{\circ}$  (that is,  $1.86^{\circ} \times 0.5$ ); if 2 moles is dissolved, the amount is  $3.72^{\circ}$  (that is,  $1.86^{\circ} \times 2$ ); etc. The amount by which the freezing point is lowered by dissolving 1 mole of a nonelectrolyte in 1 kg of a solvent is called the **molal freezing-point constant** of the solvent. The values of this constant for three solvents are:

solvent	freezing point of pure solvent, $^{\circ}\text{C}$	molal freezing-point constant, $^{\circ}\text{C}$
water	0.00	1.86
hydrogen acetate	16.60	3.90
benzene	5.48	4.90

**PROBLEM 6** Calculate the freezing point of a solution that contains 2 g of wood alcohol,  $\text{CH}_3\text{OH}$ , in 50 g of water.

*Solution* Because the amount of change in the freezing point is determined by the molality, we first calculate the molality of the solution. The molar weight of  $\text{CH}_3\text{OH}$  is 32 g.

By definition,

$$\begin{aligned}\text{molality} &= \frac{\text{no. moles}}{1 \text{ kg of solvent}} \\ &= \frac{2 \text{ g CH}_3\text{OH} / (32 \text{ g CH}_3\text{OH/mole})}{50 \text{ g solvent (1 kg/1,000 g)}} \\ &= 1.25 \frac{\text{moles}}{\text{kg solvent}} = 1.25 \text{ m}\end{aligned}$$

A 1 molal solution has a freezing-point depression of  $1.86^{\circ}$ ; a 1.25 molal solution has a proportionately larger depression:

$$\frac{1.86^{\circ}}{1 \text{ m}} \times 1.25 \text{ m} = 2.32^{\circ} \text{ lowering of fp}$$

Subtracting the amount of lowering from the freezing point of pure water gives the freezing point of the solution:

$$0^{\circ} - 2.32^{\circ} = -2.32^{\circ}\text{C}$$

The freezing point of the solution containing 2 g of wood alcohol in 50 g of water is  $-2.32^{\circ}\text{C}$ .

## VAPOR PRESSURE AND BOILING POINT OF SOLUTIONS OF NONELECTROLYTES

The boiling point of a solution may be higher or lower than that of the solvent, depending on the volatility of the solute as compared with that of the solvent. If the solute is nonvolatile—sugar is an example—its water solution boils at a temperature higher than water boils; if the solute is quite volatile—for example, alcohol—its water solution boils at a temperature below the boiling point of water (Fig. 10-13).

## SOLUTIONS

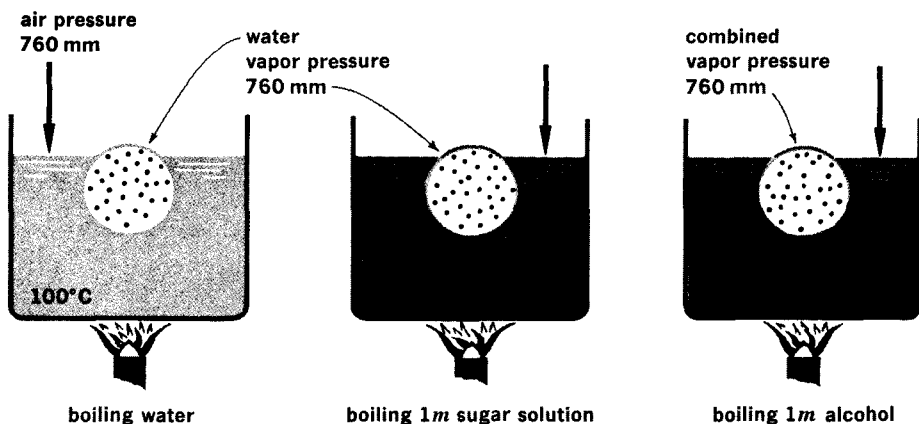


FIG. 10-13 A schematic representation of a vapor bubble in boiling water, in boiling sugar solution, and in boiling alcohol solution.

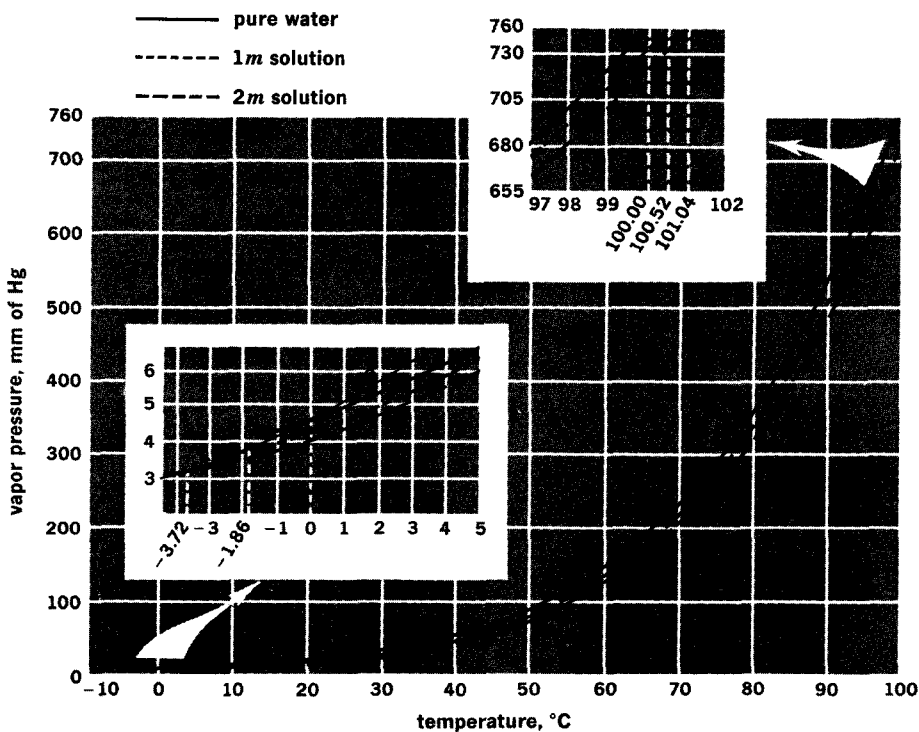


FIG. 10-14 Comparison of the vapor pressures of pure water, a one molal (1 m) solution, and a two molal (2 m) solution. The two insets show in more detail the behavior in the vicinity of the melting and boiling points.

Consideration of the kinetic theory and the definition of the boiling point make clear why these differences exist. It will be remembered that the boiling point is the temperature at which the vapor pressure of a liquid equals the atmospheric pressure. For pure water, the boiling point is  $100^{\circ}\text{C}$  when the atmospheric pressure is 760 mm. But when the temperature of an aqueous sugar solution is  $100^{\circ}\text{C}$ , the vapor pressure of the water is less than 760 mm. This is due to the fact that the sugar molecules occupy a considerable portion of a unit volume and hence decrease the concentration of water molecules. The vapor pressure of a sugar solution is therefore less than that of pure water at the same temperature; consequently the solution must be heated to a temperature higher than  $100^{\circ}$  before it boils (before the vapor pressure reaches 760 mm).

In the case of the alcohol solution, the presence of the alcohol molecules also lessens the concentration of the water molecules, so that the pressure due to water vapor is lower than that for pure water at the same temperature. However, liquid alcohol has a greater tendency to become a vapor than does water. For this reason, the vapor pressure of the solution (the sum of the alcohol pressure and the water vapor pressure) equals the atmospheric pressure at a temperature below  $100^{\circ}\text{C}$ . The boiling point of the solution is below that of pure water. The colligative property law is applicable in predicting the boiling point of solutions involving nonvolatile, nonelectrolytic solutes. The amount by which the vapor pressure is decreased and the boiling point is increased is directly proportional to the number of molecules of solute in a given quantity of solvent (Fig. 10-14).<sup>1</sup> If the number of solute molecules is  $6.02 \times 10^{23}$  (1 mole) and the amount of solvent is 1 kg, the elevation of the boiling point of water is  $0.52^{\circ}\text{C}$ . This is the **molal boiling-point constant** for water.

**PROBLEM 7** Calculate the boiling point of a solution that contains 1.5 g of glycerin,  $\text{C}_3\text{H}_8\text{O}_3$ , in 30 g of water.

**Solution** Because the amount of change in the boiling point depends on the molality, we first calculate the molality of the solution:

$$m = \frac{\text{moles of solute}}{\text{kg of solvent}}$$

$$= \frac{1.5 \text{ g} \times 1 \text{ mole}/92 \text{ g}}{30 \text{ g H}_2\text{O} \times 1 \text{ kg}/1,000 \text{ g H}_2\text{O}} = 0.54 \frac{\text{mole}}{\text{kg solvent}} = 0.54 m$$

<sup>1</sup> In the expanded graph (Fig. 10-14) showing the equilibria between ice, water, and water vapor, it is assumed that the equilibria are established in contact with air at a total pressure of 1 atm. Variations in air pressure affect the freezing point of water and water solutions slightly, both because of the change in the solubility of air in water and because of the influence of pressure on the change of state. Because water expands on freezing, an increase in pressure tends to prevent the expansion; that is, the freezing point is depressed (see Le Chatelier's principle). Dissolved air also lowers the freezing point. If the air pressure is reduced to zero (nothing is present but water), the equilibrium between the liquid, solid, and vapor phases of water becomes established at  $0.0099^{\circ}\text{C}$  (the triple point). The absence of dissolved air causes the freezing point to rise by  $0.0024^{\circ}$ , and the drop of pressure from 760 mm to a water vapor pressure of 4.57 mm causes an additional rise of  $0.0075^{\circ}$ , that is, a total rise from  $0^{\circ}$  to  $0.0099^{\circ}\text{C}$ .



A 1 molal solution has a boiling-point elevation of  $0.52^\circ$ ; a 0.54 molal solution has a proportionately lower elevation:

$$\frac{0.52^\circ}{1\ m} \times 0.54\ m = 0.28^\circ \text{ rise in bp}$$

The elevation of the boiling point is  $0.28^\circ$ . The boiling point is

$$100^\circ + 0.28^\circ = 100.28^\circ\text{C}$$

**Experimental Determination of Molecular Weights.** One method of arriving at molecular weights is based on Avogadro's law. Experimentally, the problem is to find the weight of 22.4 liters of gas at standard conditions. This amount of gas contains 1 mole and its weight in grams is equal numerically to the molecular weight. (This was discussed in Chap. 8.)

A second method of arriving at molecular weights is based on the colligative property law. Experimentally, the problem is to find the weight of solute needed to lower the freezing point of 1 kg of solvent by the molal freezing-point constant (or the weight needed to raise the boiling point of 1 kg of solvent by the molal boiling-point constant). This weight of solute contains 1 mole and its weight in grams is equal numerically to the molecular weight.

When a new compound is discovered—new ones are being discovered every day—it is of great interest to find the weight of one molecule. In order to do this, it is only necessary to measure the amount of the new compound needed to lower the freezing point of 1 kg of water by  $1.86^\circ$  or to elevate the boiling point by  $0.52^\circ$ . In actual laboratory work it is not practical to use 1 kg of water and then dissolve small portions of the new compound, testing the freezing point after each addition till the amount needed to lower the freezing point by  $1.86^\circ$  is found. Instead, a single solution is carefully made, and the freezing point of this solution is accurately determined. From the data thus obtained the necessary calculations can be made. The following problem illustrates the method.

**PROBLEM 8** A solution made by dissolving 0.320 g of a new compound Z in 25.0 g of water has a freezing point of  $-0.201^\circ\text{C}$ . Calculate the molecular weight of the new compound.

**Solution** Let us begin by calculating the molality of the solution. The change in freezing point,  $\Delta_{\text{fp}}$ , is  $0.201^\circ\text{C}$ , that is,  $0^\circ\text{C} - (-0.201^\circ\text{C})$ . Because 1 mole of solute in 1 kg of water lowers the freezing point  $1.86^\circ$ , it is apparent that the solution of Z is less than one molal:

$$\begin{aligned} \text{molality of solution} &= \frac{\Delta_{\text{fp}}}{\text{molal freezing-point constant}} \\ &= \frac{0.201^\circ}{1.86^\circ/1\ m} = 0.108\ m \end{aligned}$$

$$\text{wt solute} = (\text{molality})(\text{no. kg solvent})(\text{wt of 1 mole solute})$$

$$0.320 \text{ g Z} = \left(0.108 \frac{\text{mole}}{1 \text{ kg}}\right) \left(25.0 \text{ g} \times \frac{1 \text{ kg}}{1,000 \text{ g}}\right) (\text{wt of 1 mole solute Z})$$

$$\text{wt of 1 mole solute Z} = \frac{0.320 \text{ g Z}}{0.108 \text{ mole} \times 0.0250}$$

$$= 118 \text{ g/mole}$$

$$\text{therefore, mol. wt} = 118 \text{ awu}$$

## PROPERTIES OF SOLUTIONS OF ELECTROLYTES

It has been emphasized that the extent to which the freezing point, boiling point, and vapor pressure differ from those of the pure solvent depends on the number of solute particles (molecules, atoms, or ions) in a given weight of the solvent. With nonelectrolytes, 1 mole refers to the same number of particles, namely,  $6.02 \times 10^{23}$  molecules. But in the case of an electrolyte 1 mole refers to a larger number of particles. The "apparent" molecule, NaCl, is not a molecule but a pair of ions,  $\text{Na}^+$ ,  $\text{Cl}^-$ . This means that 58.5 g of NaCl contains, not  $6.02 \times 10^{23}$  molecules, but  $6.02 \times 10^{23}$   $\text{Na}^+$  ions and  $6.02 \times 10^{23}$   $\text{Cl}^-$  ions. The data in Table 10-2 show that for the electrovalent type of electrolyte, the number of particles in a mole is twice, three times, four times, etc., the number in a mole of a covalent compound.

### *Particles per mole for electrolytes*

TABLE 10-2

formula	particles represented by formula	weight of 1 mole, g	no. of particles in 1 mole
NaCl	$\text{Na}^+$ , $\text{Cl}^-$	58.5	$2 \times 6.02 \times 10^{23}$
$\text{KNO}_3$	$\text{K}^+$ , $\text{NO}_3^-$	101.0	$2 \times 6.02 \times 10^{23}$
$\text{CaCl}_2$	$\text{Ca}^{2+}$ , $\text{Cl}^-$ , $\text{Cl}^-$	111.0	$3 \times 6.02 \times 10^{23}$
$\text{Na}_2\text{SO}_4$	$\text{Na}^+$ , $\text{Na}^+$ , $\text{SO}_4^{2-}$	142.0	$3 \times 6.02 \times 10^{23}$
$\text{AlF}_3$	$\text{Al}^{3+}$ , $\text{F}^-$ , $\text{F}^-$ , $\text{F}^-$	84.0	$4 \times 6.02 \times 10^{23}$

When 1 mole of an electrovalent type of electrolyte is dissolved in 1 kg of water, the amounts by which the freezing and boiling points are changed are considerably more than  $1.86^\circ$  and  $0.52^\circ$ , respectively. Indeed, it appears at first glance that these constants would be exactly doubled for such compounds as sodium chloride,  $\text{Na}^+$ ,  $\text{Cl}^-$ , and potassium nitrate,  $\text{K}^+$ ,  $\text{NO}_3^-$ , and exactly tripled for such compounds as calcium chloride,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Cl}^-$ , and sodium sulfate,  $\text{Na}^+$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ . Laboratory experiments show that this is not the case. The explanation is believed to lie in the fact that each ion strongly attracts the oppositely charged ions in its vicinity, so that no ion can act completely as an independent particle. These interionic attractions are reduced to a minimum when the solution is very dilute, because the ions are separated by many water molecules. Consequently, the ob-

served changes in the freezing and boiling points of very dilute solutions of KCl, NaCl, and  $\text{MgSO}_4$  approach twice those in a solution of a nonelectrolyte of the same molal concentration, and the change for  $\text{K}_2\text{SO}_4$  approaches three times the change for a nonelectrolyte.

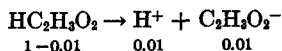
Table 10-3 shows how many times greater the observed freezing-point depression is than that for a non-electrolyte in a solution of the same concentration.

**TABLE 10-3** *Comparison of freezing-point lowering by electrovalent electrolytes with lowering by nonelectrolytes*

electrovalent type of electrolyte	comparison at the molal concentrations indicated				no. of ions per apparent molecule
	0.10	0.050	0.010	0.005	
NaCl	1.87	1.89	1.93	1.94	2
KCl	1.86	1.88	1.94	1.96	2
$\text{MgSO}_4$	1.42	1.43	1.62	1.69	2
$\text{K}_2\text{SO}_4$	2.46	2.57	2.77	2.86	3

For example, a 0.10 molal NaCl solution freezes at  $-0.348^\circ$ , and a 0.10 molal sugar solution freezes at  $-0.186^\circ$ . This means that the freezing-point depression of NaCl is  $\frac{0.348}{0.186}$ , or 1.87 times the depression of sugar, when the solutions are both 0.10 molal. Observe that the numbers in the 0.005 molal concentration column (very dilute) are approaching 2 or 3, respectively.

**Number of Particles in Solutions of Covalent Electrolytes.** You will remember that pure hydrogen acetate and hydrogen chloride are not electrolytes till they are dissolved in water. The total number of particles resulting when 1 mole of one of these or some other covalent electrolyte is added to water is not predictable from the formula, unless the extent to which ionization occurs is known. For example, if 1 molal acetic acid is 1 per cent ionized, the total number of solute particles per kilogram of water corresponds to 1.01 moles of particles ( $6.08 \times 10^{23}$  molecules and ions):



Total moles of particles:

$$1 - 0.01 + 0.01 + 0.01 = 1.01 \text{ moles}$$

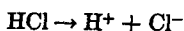
The calculated lowering of the freezing point is  $1.88^\circ$  (that is, 1.01 moles  $\times 1.86^\circ/\text{mole}$ ). The data in Table 10-4 show how many times greater the observed freezing-point depressions are for electrolytes than the depressions produced by nonelectrolytes at the same molal concentration. Thus a 0.005 molal sulfuric acid solution gives a freezing-point lowering 2.72 times that for a nonelectrolyte at the same molal concentration.

*Comparison of freezing-point lowering by covalent electrolytes with lowering by nonelectrolytes*

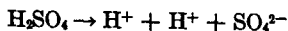
TABLE 10-4

covalent type of electrolyte	comparison at the molal concentrations indicated				theoretical no. of ions formed from each molecule
	0.10	0.050	0.010	0.005	
HCl	1.91	1.92	1.97	1.99	2
HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	1.01	1.02	1.05	1.06	2
H <sub>2</sub> SO <sub>4</sub>	2.22	2.32	2.59	2.72	3

It will be observed that hydrogen chloride has almost twice the effect on the freezing point that a nonelectrolyte does. This indicates that hydrogen chloride is essentially 100 per cent ionized in water solutions that are not too concentrated:



Very dilute sulfuric acid solutions are also essentially 100 per cent ionized (Table 10-4).



Again, the lowering of the freezing point is not exactly that calculated on the basis of the number of ions because of interionic attractions.

A dissolved electrolyte that is present completely as ions (or almost so) is called a **strong electrolyte**. Examples include the four compounds listed in Table 10-3 and all other electrovalent compounds. Also included are substances such as hydrochloric acid and sulfuric acid in Table 10-4. Hydrochloric, nitric, and sulfuric acids are said to be **strong acids**, because they are highly ionized in dilute solutions.

A dissolved electrolyte that is present even in dilute solutions largely as un-ionized molecules is a **weak electrolyte**. Acetic acid, HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, is a weak acid (Table 10-4). Even at a dilution of 0.005 *m*, the effect of acetic acid on the freezing point shows that few ions are present.

## IDEAL SOLUTIONS

Thus far the discussion has indicated that in solutions of nonelectrolytes, the magnitude of the changes in the freezing point and other properties depends solely on the number of particles, whereas in solutions of electrolytes, the magnitude of the change depends on two factors: namely, the number of particles and the interionic attractions. Actually,  $6.02 \times 10^{23}$  solute molecules of different substances do not produce exactly the same change in the properties of solutions. We think the reason for this is that intermolecular attraction is present in solutions of nonelectrolytes. However, this van der Waals attrac-

tion of solute molecules for each other and for solvent molecules has so slight an effect that no great deviations in the freezing-point and boiling-point constants are produced unless the solutions are concentrated. Dilute solutions act ideally in that we need to consider only the number of molecules or ions present, and not their nature, in calculating changes in properties. The data in Table 10-5 show the magnitude of deviation for four moderately concentrated solutions.

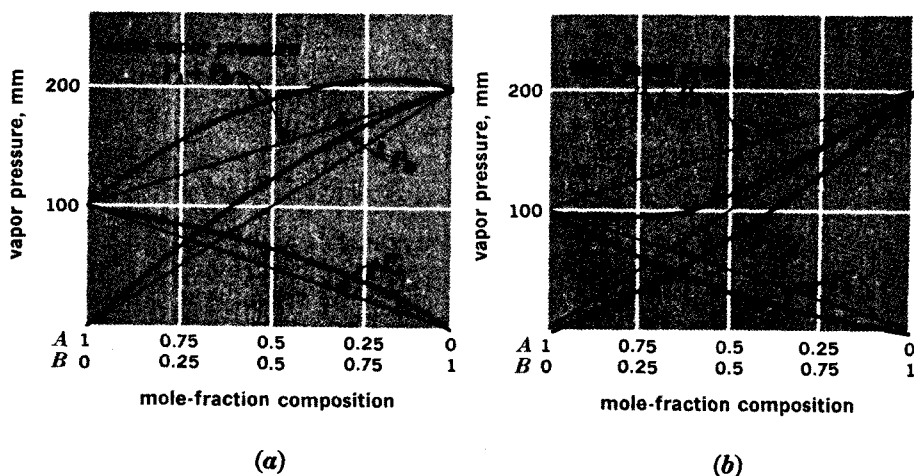
TABLE 10-5 *Experimental molal freezing-point depressions*

solute	formula	molar weight, g	observed freezing-point depression for 1 mole in 1 kg of water, °C
Methyl alcohol	$\text{CH}_3\text{OH}$	32	1.86
Ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$	46	1.83
Glycerin	$\text{C}_3\text{H}_8(\text{OH})_3$	92	1.92
Urea	$\text{CO}(\text{NH}_2)_2$	60	1.86

## DISTILLATION

**Vapor Pressure.** Consider two hypothetical liquids, *A* and *B*, that are completely miscible with each other. Let us imagine that we have measured the vapor pressure of each pure liquid at 20° and found it to be 100 mm for *A* and 200 mm for *B*. We can use these vapor pressures to calculate the vapor pressure of a solution of *A* and *B* for any concentration that we might make, provided the solution acts ideally. For example, if we dissolve  $\frac{1}{4}$  mole of *A* in  $\frac{3}{4}$  mole of *B*, the mole-fraction of *A* in the solution is 0.25, and the pressure of its vapor in equilibrium with the solution according to Raoult's law is (0.25) (100 mm) or 25 mm. Similarly, the vapor pressure of *B* is (0.75) (200 mm) or 150 mm. The vapor pressure of the solution equals the sum of the partial pressures of *A* and *B*, 25 mm + 150 mm, or 175 mm. In another solution, in which the mole fraction of *A* is 0.50, the partial vapor pressures for *A* and *B* are 50 mm and 100 mm, respectively, and the vapor pressure of the solution is 150 mm. The black lines of Fig. 10-15 show the ideal vapor pressure and the partial pressures of *A* and *B* for solutions of all concentrations of *A* and *B*.

Real liquids do not behave ideally, so that the measured vapor pressures of a liquid mixture may differ from slightly to a large amount from that calculated by Raoult's law. For some pairs, the attractions of molecules of *A* for one another and molecules of *B* for one another exceed the attractions of molecules of *A* for molecules of *B*. The overall result is that *A* molecules tend to "force" *B* molecules from the solution, and vice versa. In this case the actual vapor pressure exceeds the ideal pressure, and we have a *positive deviation* from Raoult's law, as shown by the blue lines in Fig. 10-15*a*. Examples of such liquid pairs are ethyl alcohol and water, carbon tetrachloride and ethyl alcohol, and acetone and methanol.



(a) A vapor pressure graph showing a positive deviation (blue lines) from ideal behavior (black lines). (b) A negative deviation (blue lines) from ideal behavior (black lines) is shown in this plot.

FIG. 10-15

When molecules of *A* and *B* attract one another strongly as compared with the attractions of *A* for *A* and *B* for *B*, molecules of *A* and *B* have a smaller tendency to break away from the solution and go into the vapor state. In such cases the actual vapor pressures are less than the ideal ones, and we have a *negative deviation* from Raoult's law, as shown by the blue lines of Fig. 10-15b. Some actual liquid pairs that have a negative deviation are water and nitric acid, and water and acetic acid.

**Fractional Distillation.** When a mixture of two miscible liquids is boiled, the vapor that escapes from the liquid usually has a different composition than that of the boiling liquid. The common behavior is for the vapor to be richer (more concentrated) in the more volatile component. By boiling away part of the liquid and condensing the vapor, the mixture can be separated into two parts: the *distillate*, which is richer than the original liquid in the more volatile component, and the *residue*, which is richer in the less volatile component.

By preparing liquid mixtures of different compositions and measuring the boiling points and the compositions of the vapors that distill first, one can plot two distillation curves that show the composition of the liquid and the vapor at any boiling point. Consider the curves shown in Fig. 10-16 for mixtures of two hypothetical liquids *A* and *B*, whose individual boiling points are 50° and 100°, respectively. A horizontal line drawn at any boiling point between 50° and 100° intersects both the liquid composition curve and the vapor composition curve. The horizontal line at a bp of 66° intersects the liquid curve at mole fractions of 0.50 *A* and 0.50 *B*, as shown by

points  $n$  and  $n'$ ; the composition of the vapor at this bp is 0.84  $A$  and 0.16  $B$ , as shown by points  $m$  and  $m'$ .

The effect of continually boiling away a liquid that has the original composition 0.50  $A$  and 0.50  $B$  is shown by Fig. 10-16. Because the escaping vapor is richer in  $A$ , the liquid left behind becomes increasingly richer in  $B$ . As the mole fraction of  $B$  in the liquid residue increases, the bp rises above  $66^\circ$ , as we can see by moving along the lower curve to the right and upward in Fig. 10-16.

In time, the mole fraction of  $A$  in the liquid remaining is reduced to some small value, say 0.05; the mole fraction of  $B$  is then 0.95 (point  $y$  in Fig. 10-16); and the boiling point has climbed close to that of  $B$ .

It is apparent from a consideration of the composition of the vapor that comes off at the beginning of the distillation (point  $m$  of Fig. 10-16) and that which comes off toward the end (point  $x$ ) that  $A$  and  $B$  cannot be obtained as pure liquids by a simple distillation, such as is illustrated in Fig. 1-3.

To bring about a better separation of  $A$  and  $B$ , the distillate can be collected in fractions, and each fraction redistilled into fractions, and so on. Eventually, a first fraction is obtained that approaches 100 per cent  $A$ , and a last fraction that approaches 100 per cent  $B$ . This process is one type of **fractional distillation**. It is called a *batch process*, because each part of the collected mixture is handled as a separate batch.

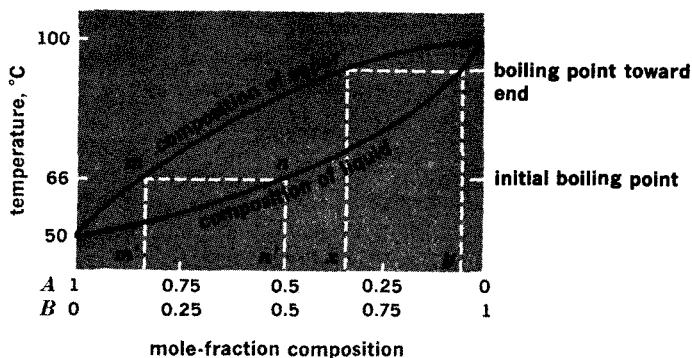


FIG. 10-16

A graph showing how the boiling point and the composition of vapor and liquid change as a solution of two liquids with approximately ideal behavior is distilled. Note that such a liquid mixture cannot be separated into pure  $A$  and pure  $B$  by a single distillation.

Chemical and physical separations are relatively tedious and inefficient when carried out as batch processes. It is often possible to effect separations by an efficient *continuous process*. A continuous series of distillations, condensations, redistillations, recondensations, and so on, can be carried out in an expeditious manner by the use of **fractionating columns**, so designed that the vapor condenses and re-

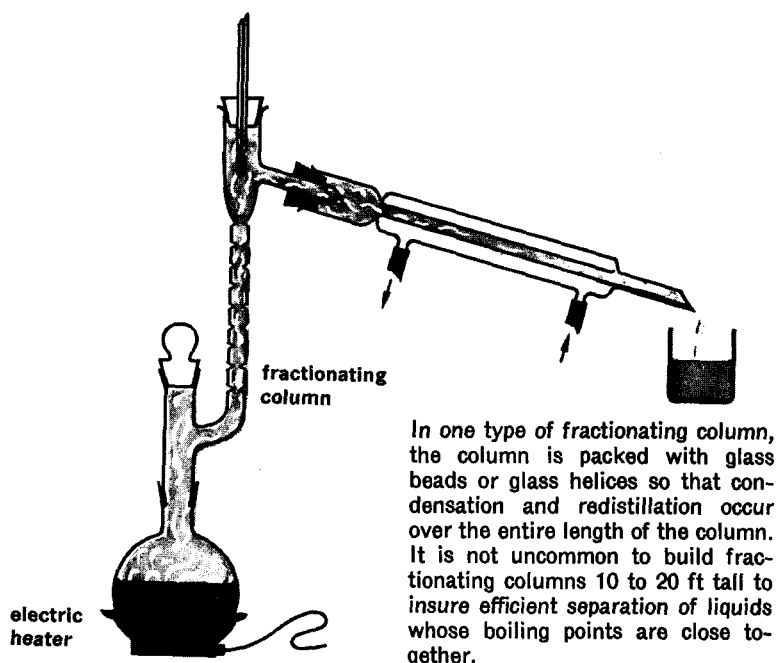


FIG. 10-17

distills many times before leaving the column. Fractionating columns, to be efficient, must provide good contact between the ascending vapor and the descending liquid formed by the condensation of vapor. With an efficient column, essentially pure *A* is obtained as the first fraction and pure *B* as the last. One design is shown in Fig. 10-17.

**CONSTANT-BOILING MIXTURES.** If the composition of the vapor distilling from a liquid mixture is the same as the liquid phase, the composition of the mixture does not change on boiling, and the boiling point does not change. Such a mixture is called a **constant-boiling mixture**. Mixtures whose vapor pressures vary greatly enough from ideal behavior may form constant-boiling mixtures.

Figure 10-18*a* shows the type of composition change expected during the distillation of liquid systems that form constant-boiling mixtures with boiling points below those of either component. Water and ethyl alcohol, acetone and methanol, and ethyl acetate and water are examples of mixtures with *minimum boiling points* that have distillation curves of the general pattern of Fig. 10-18*a*.

Figure 10-18*b* represents the composition changes for the distillation of solutions that form constant-boiling mixtures with a boiling point above that of either component. Some examples of constant-boiling mixtures with *maximum boiling points* are water and nitric acid, water and acetic acid, and acetic acid and ethyl amine.

When systems forming minimum boiling-point mixtures are distilled from *efficient fractionating columns*, the first distillate tends to



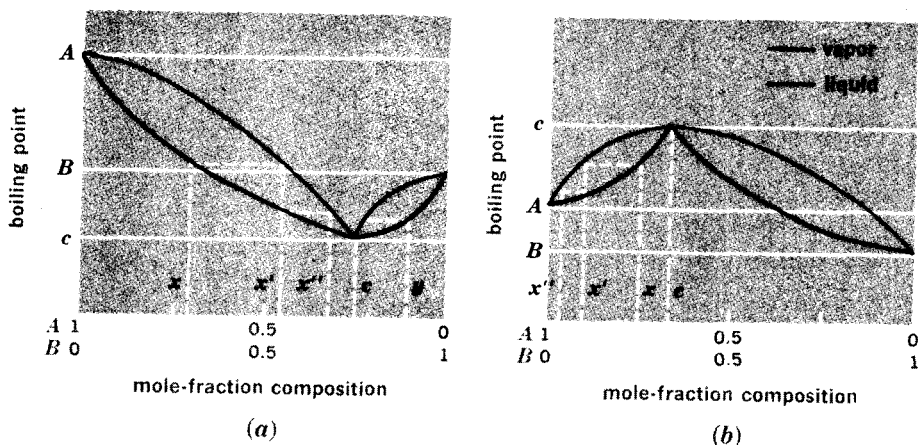


FIG. 10-18

(a) Graph showing the changes in composition and boiling point during the distillation of two miscible liquids which form a constant boiling mixture with a boiling point below that of either component. (b) Graph showing similar changes for distillation of two liquids which form a constant boiling mixture with a maximum boiling point.

have the composition of the *constant-boiling mixture*, represented by  $c$  in Fig. 10-18a; the liquid left in the distilling flask, or that which distills last, tends to have the composition of pure  $A$  or of pure  $B$ , depending on the composition of the original mixture. That is, the fractional distillation of a mixture having the composition represented by  $x$  tends to produce pure  $A$  as the last fraction; a mixture represented by  $y$  tends to produce pure  $B$  (the first fraction in both cases is the constant-boiling mixture).

The efficient fractional distillation of maximum-boiling mixtures tends to produce either  $A$  or  $B$ , depending on the initial composition, as the first distillate, and to leave the constant-boiling mixture behind. For example, if a mixture of 10 per cent  $\text{HNO}_3$  (bp  $86^\circ$ ) and 90 per cent  $\text{H}_2\text{O}$  (bp  $100^\circ$ ) is fractionally distilled, pure water comes over till the composition of the liquid remaining reaches 32 per cent  $\text{H}_2\text{O}$  and 68 per cent  $\text{HNO}_3$ . The two then distill as a single component, and the boiling point ( $120.5^\circ\text{C}$ ) remains constant during the rest of the distillation. (See Fig. 10-18b and imagine that  $A$  is  $\text{H}_2\text{O}$  and  $B$  is  $\text{HNO}_3$ .) Had we started with 90 per cent  $\text{HNO}_3$  and 10 per cent  $\text{H}_2\text{O}$ , pure  $\text{HNO}_3$  would have distilled till the composition of the boiling liquid had changed to 68 per cent  $\text{HNO}_3$  and 32 per cent  $\text{H}_2\text{O}$ . The two would then distill together as in the previous example.

In summary, when solutions of liquids that form constant-boiling mixtures are distilled in efficient fractionating apparatus, the constant-boiling mixture tends to distill first if it has a boiling point below that of either pure component and to distill last if its boiling point is higher than that of either pure component.

## OSMOSIS

If pure water is separated from a water solution by a membrane through which only water molecules can pass, the water diffuses through the membrane from the pure solvent into the solution more rapidly than it does from the solution into the pure solvent. A membrane that permits the passage of only certain types of molecules is called a **semipermeable membrane**; the passing of the solvent through the membrane is called **osmosis**. Osmosis may be readily demonstrated by fastening a piece of animal bladder or nonwaterproof cellophane over a thistle tube, as shown in Fig. 10-19. An aqueous sugar solution is placed inside the thistle tube, which is then immersed in water. At the beginning, water molecules pass more rapidly from the pure water into the sugar solution than in the opposite direction. Because of this unequal rate, water accumulates in the thistle tube, and the water level in it rises. As time goes on, the sugar solution becomes more and more dilute; consequently, the rate at which the water molecules pass back into the solvent steadily increases. The increase in rate is also due to the increasing pressure in the water column. In time, the rate of flow in both directions becomes the same, and the water level ceases to rise. Actually this is very difficult to achieve, because as the water level rises, the pressure of the solution on the membrane may increase till the membrane splits and spills the solution into the solvent.

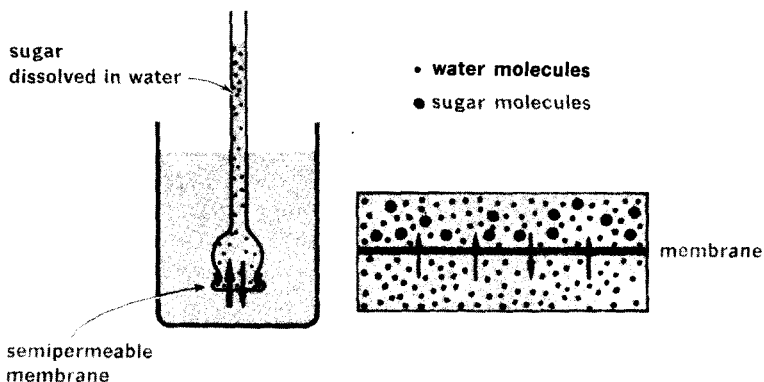


FIG. 10-19

## Osmosis.

**Osmotic Pressure.** The **osmotic pressure** of a solution is defined as the pressure required to prevent any increase in volume of a solution by the transfer of pure solvent into it through a semipermeable membrane. To measure the osmotic pressure in the laboratory, a sturdy apparatus of the type shown in Fig. 10-20 is employed. The solution is placed in a steel or other strong vessel that will not stretch or burst because of the additional molecules that crowd in.

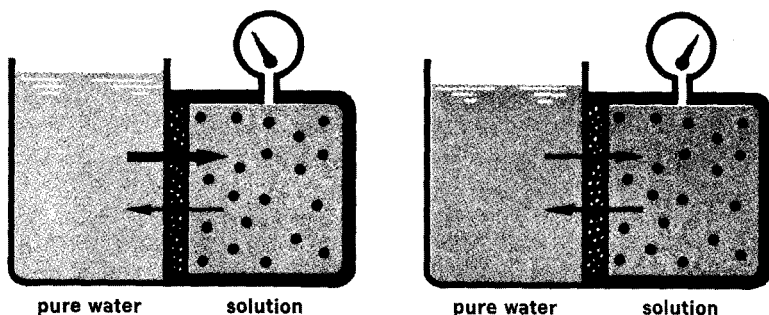


FIG. 10-20

Apparatus for measuring osmotic pressure.

The semipermeable membrane is actually a thick wall of an inorganic material that permits the passage of water molecules but not solute molecules. On the other side of this membrane is pure water. At the outset of the experiment water molecules pass more rapidly into the solution than out of it because of the unequal concentration of water on the two sides of the membrane. In time, the pressure built up by the crowding of more molecules into the fixed volume is sufficiently great to offset the effect produced by the unequal concentration, and the rates of flow in and out become the same. The gauge reading is the osmotic pressure of the solution.

**Biological Importance of Osmosis.** Osmosis is of great importance to plants and animals, because it is the process by which water is distributed to all the cells of living organisms. Cell walls are semipermeable membranes through which water passes in both directions in accordance with the principles discussed in the preceding paragraphs. The membranes of living cells are also permeable to certain solutes so that nutrients and waste products are exchanged through them. The permeability of cell walls to solutes is frequently selective and to some extent independent of the size of the solute particles and to concentrations. For example, small magnesium ions do not pass through the walls of the gastrointestinal tract to any great extent, whereas much larger glucose molecules pass through at a rate too rapid to be accounted for by simple diffusion.

When solutions to be injected into the blood stream are made up, the osmotic pressure of the solution has to be considered. The average osmotic pressure of the blood is about 7.7 atm (it rises just after meals, then falls). If red blood cells are placed in a solution that has a greater osmotic pressure than that of normal blood, water passes out of the cells till they shrink and settle out of suspension. If the cells are put into a solution that has a lower osmotic pressure than blood, the cells may swell with water till the cell walls burst. Consequently,

the osmotic pressure of solutions for injection is adjusted (chiefly with sodium chloride) till it is compatible<sup>1</sup> with blood.

## CHAPTER REVIEW

### Terms

Solution, homogeneous, heterogeneous, solute, solvent, solvation, dielectric constant, entropy, insoluble, immiscible, saturated, unsaturated, supersaturated, solubility,  $\Delta H_{soln}$ , Le Chatelier's principle, Henry's law, molarity, molality, mole fraction, normality, titration, standard solution, indicators, colligative properties, Raoult's law, molal freezing- and boiling-point constants, strong and weak electrolytes, ideal solution, distillation, fractional distillation, distillate, residue, constant-boiling mixture, osmotic pressure, semipermeable membrane.

### Exercises

1. Compare theoretically the mechanism of the dissolving of a covalent versus an ionic substance in water.
2. a. Why should 12-carat gold be called a solution rather than a compound?  
b. In 12-carat gold what is the solute and what the solvent?
3. "Pure air, free of extraneous particles, is a solution." Discuss the validity of this statement.
4. "Iron dissolves in sulfuric acid." Do you think this is a proper statement? Why?
5. Potassium iodide is more soluble in methyl alcohol than in benzene, whereas lubricating oil is more soluble in benzene. Suggest explanations for both cases.
6. Explain, using diagrams, how it is possible for the process



to result in an increase in entropy in one case but a decrease in another, especially if one of the solutes consists of ions that strongly attract water molecules.

7. Water and alcohol are miscible, but water and carbon tetrachloride are immiscible. Correlate this behavior with the molecular structures of the three compounds.
8. a. Would it be possible to make a saturated or supersaturated solution using two immiscible liquids, say ether in water?  
b. Repeat (a) for the case of two miscible liquids.

<sup>1</sup> In biological and medical terminology, solutions that have the same osmotic pressure as blood are called **isotonic** solutions; those which have smaller osmotic pressures are called **hypotonic** solutions; and those which have larger osmotic pressures are called **hypertonic** solutions.

9. When a solid substance dissolves, two processes are of prime importance: the breaking away of particles from the solid and the joining of solute and solvent particles. In terms of these two processes, tell how the dissolving in water of sodium hydroxide can be exothermic, whereas for ammonium chloride the process is endothermic.
10. Although pressure changes have only a very slight effect on the solubility of salts, consider the case of lithium fluoride. A solution of this salt occupies less volume than the salt and water separately. What effect does an increase in pressure have on the solubility of lithium fluoride? Explain.
11. G. Cseko and I. Cornides report in the *Journal of Inorganic and Nuclear Chemistry*, **14**: 139-141 (1960), the following data for the solubility of argon in liquid ammonia:

pressure, atm	cc Ar/g NH <sub>3</sub>
25	3.58
50	8.69
75	13.10
100	18.20

Show by calculation and by a graphical method that the data agree or do not agree with the appropriate law.

12. Calculate the weight of water in a liter of 98 per cent sulfuric acid that has a density of 1.82 g/ml.
13. How many moles of copper sulfate are there per 100 ml of a 2.0 per cent solution? Assume a density of unity.
14. What is the weight of alcohol in grams in a quart of wine that is 12 per cent alcohol by volume; 12 per cent alcohol by weight? The density of the solution is 0.984 g/ml, of pure alcohol is 0.789 g/ml, and of water is 1.000 g/ml.
15. What weight of glycerin would there be in 175 ml of a 0.30 *M* solution? How many moles of glycerin? How many glycerin molecules?
16. a. Calculate the weight of H<sub>2</sub>SO<sub>4</sub> in 200 ml of a 3.2 molar solution.  
b. Calculate the normality of the H<sub>2</sub>SO<sub>4</sub> solution.
17. a. How many milliliters of a 0.25 *M* solution of sodium hydroxide are needed to neutralize 100 ml of a 0.40 *M* sulfuric acid solution?  
b. How many moles of H<sub>2</sub>SO<sub>4</sub> are dissolved in the sulfuric acid solution?  
c. How many moles of NaOH are needed to react with the sulfuric acid?  
d. What weight of sodium sulfate is formed (in solution, that is)?
18. When silver nitrate, AgNO<sub>3</sub>, was added in excess to 25.0 ml of an HCl solution of unknown concentration, a precipitate of silver chloride, AgCl, formed that, when dried, was found to weigh 0.538 g. Calculate the molarity of the HCl solution, assuming that all the chloride ion present precipitated in the AgCl.
19. In preparing a concentrated solution of hydrochloric acid, 60 g of HCl was dissolved in 100 g of water to form 133 ml of solution. Calculate the following.

- a. The density of the solution
  - b. The percentage composition by weight
  - c. The molarity of the solution
  - d. The molality of the solution
  - e. The normality of the solution
  - f. The mole fractions of solute and solvent
20. a. Knowing the solute and solvent, and given the molarity of a solution, can the percentage of solute by weight be calculated? Illustrate with an example.
- b. Repeat (a), given the molality.
21. a. Knowing the solute and solvent, and given the molarity of a solution, can the mole fraction of solute be calculated? Illustrate with an example.
- b. Repeat (a), given the molality.
22. a. How many equivalent weights of KOH are there in 26 ml of a 0.48 *N* solution; of  $\text{H}_2\text{SO}_4$  in 26 ml of a 0.48 *N* solution; of  $\text{Ba}(\text{OH})_2$  in 26 ml of a 0.48 *N* solution?
- b. For each part of (a) calculate the moles of solute present and the weight of solute in grams.
23. How much of a 0.234 *N* solution of  $\text{H}_2\text{SO}_4$  has to be diluted in order to prepare a liter of 0.100 *N* acid?
24. A sample of a metal weighing 0.0730 g reacted completely when allowed to stand in 100 ml of 0.1000 *N* HCl. The excess acid was neutralized by titration with 32.0 ml of 0.125 *N* KOH. Calculate the equivalent weight of the metal.
25. To analyze some concentrated sulfuric acid, a 5.00-ml sample of the acid was diluted to a liter; then a 25.00-ml sample of the diluted acid was titrated with 0.1000 *N* NaOH. It required 18.75 ml of the base to neutralize the sample of dilute acid. Calculate the normality and molarity of the concentrated acid.
26. Suppose you wished to prepare a sample of  $\text{KHSO}_4$  by evaporating a solution of it to dryness. How much 0.125 *M*  $\text{H}_2\text{SO}_4$  would have to be added to 100 ml of 0.750 *N* KOH to prepare the starting solution?
27. A standard solution was made by dissolving 4.26 g of potassium hydrogen phthalate,  $\text{KHC}_8\text{H}_4\text{O}_4$  (a monoprotic acid), in enough water to make 100 ml of solution; 16.3 ml of this solution was required to titrate 20.3 ml of a sodium hydroxide solution; 28.4 ml of the sodium hydroxide solution was required to titrate 40.1 ml of acid solution of unknown concentration. Calculate the normality of the unknown acid solution. (Note: In order to obtain a standard base solution of NaOH, it is usually necessary to determine its concentration with a standard acid solution, because commercial NaOH contains considerable water. A direct weighing of NaOH does not give the true amount of base present.)
28. A solution of a covalent compound in water is found to have a freezing point of  $-3.0^\circ\text{C}$ .
- a. What is the molality of the solution?

- b. What is the mole fraction of solute?
  - c. Assuming the solute is nonvolatile, what is the boiling point?
  - d. Reconsider all parts of this problem, assuming that the solute is a strong electrolyte, such as  $\text{NaCl}$ ,  $\text{KNO}_3$ , or  $\text{CsF}$ .
29. Consider a hypothetical compound that is soluble in several solvents. A 1.50-g sample of the compound in 25 g of water produces a solution that freezes at  $-2.0^\circ\text{C}$ . Calculate the freezing point of a solution made by dissolving 1.50 g of this solute in 25 g of hydrogen acetate; in 25 g of benzene.
  30. What weight of ethyl alcohol,  $\text{C}_2\text{H}_5\text{OH}$ , must be added to a liter of water to yield a solution with a freezing point of  $-15^\circ\text{F}$ ?
  31. If a mixture of 12 qt of water and 10 lb of ethylene glycol,  $\text{C}_2\text{H}_4(\text{OH})_2$ , is used in an automobile radiator, what is the approximate freezing point of the solution? If 10 lb of methyl alcohol,  $\text{CH}_3\text{OH}$ , were used in place of the glycol, what would be the approximate freezing point?
  32. a. What is the molecular weight of a compound if 0.296 g dissolved in 8.00 g of benzene produces a solution that freezes at  $3.15^\circ$ ?  
b. State the assumptions, if any, you made in working (a).
  33. Calculate the vapor pressure at  $20^\circ$  of a 5.0 *m* solution of glucose (a nonelectrolyte), assuming that the vapor pressure of a solution containing a nonvolatile solute is proportional to the mole fraction of the solvent. See Table 2 in the Appendix for the needed data.
  34. Estimate the boiling points of 0.40 *m* solutions of glucose, glycerin, sodium chloride, and sulfuric acid. The first two solutes are nonelectrolytes. Mention any assumptions that you make in your calculations.
  35. To determine the molecular weight of an unknown compound, 0.500 g of it is dissolved in 50.0 g of water and the boiling point determined as  $100.056^\circ$ . Calculate the molecular weight. State any assumptions that one makes in calculating the molecular weight in this way.
  36. An aqueous solution of ethyl alcohol freezes at  $-0.56^\circ$ . What freezing temperature would you predict for a magnesium chloride solution of the same molal concentration?
  37. How can one account for the facts, listed in Table 10-2, that a 0.005 *m* solution of magnesium sulfate lowers the freezing point 1.69 times as much as does a 0.005 *m* solution of a nonelectrolyte, whereas for 0.10 *m* solutions the relative lowering is only 1.42 times?

## SUPPLEMENTARY READING

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## THE COLLOIDAL

## STATE

*Particle Size and the Colloidal State.*

The average diameter of atoms and simple ions is of the order of 2 Å, or  $2 \times 10^{-8}$  cm, as we can see in Fig. 4-15. The molecules of simple compounds, such as water, ammonia, and ethyl alcohol, are, of course, larger than atoms, but usually not many times larger if we consider only the smallest dimension of the molecule. Only when several million molecules of this type are clustered together are particles formed that can be seen by the unaided eye.

Often particles are formed that contain only a few hundred or a few thousand atoms, ions, or small molecules. The diameters of such particles may range from 10 Å ( $10^{-7}$  cm) to 1,000 Å ( $10^{-5}$  cm). Such particles cannot be seen clearly with the most powerful optical microscope.<sup>1</sup> When matter is in this state of subdivision, some interesting and important properties become evident that are not characteristic of matter when its molecules (or ions) are aggregated into larger particles.

For example, water is normally present in air as single molecules (water vapor). Under the proper atmospheric conditions, the water molecules cluster together, forming tiny droplets of water that appear as fog or clouds, but the diameter of the individual particles is roughly of the order of 10 to 1,000 Å. That water in this form has certain properties not possessed by larger masses of water is evidenced by the fact that the droplets remain suspended, although

<sup>1</sup> These minute particles are smaller than the wavelength of the visible light that they must reflect in order to be seen. The shortest wavelength of visible light is approximately 4,000 Å ( $4 \times 10^{-8}$  cm).



their density is considerably greater than that of air. Further, the droplets scatter light in all directions so that we can no longer see through them as we can when water is present in the air as single molecules (vapor) or as a liquid. When the droplets coalesce into particles with diameters somewhat larger than 1,000 Å, they can be seen with a microscope. Moreover, they begin to settle toward the earth as mist or rain.

Matter that is in a state of subdivision, with the particle size ranging from approximately 10 Å to 1,000 Å, is said to be in the **colloidal state**. The colloidal state is not characteristic of any particular substance; practically all substances, whether normally gaseous, liquid, or solid, can be put into the colloidal state.

It should be pointed out that a definition of the colloidal state based entirely on particle size is not completely satisfactory. For one thing, such a definition assumes that the particles in the specified range act as independent particles. However, in some cases the particles may group further to form larger and well-organized structures, and the material will still exhibit characteristically colloidal properties. Thus, **colloidal properties**, as well as particle size, are helpful in defining the colloidal state. Colloidal properties are discussed in a later section.

**Particle Shape.** For matter whose particles have the shape of droplets and granules, the diameter gives a measure of the particle size. For films and filaments, the length, width, and thickness are all needed to indicate the particle size. However, only one of these dimensions has to be in the range of 10 to 1,000 Å for the material to be classed as colloidal. For example, soap in a soap bubble is classed as colloidal, because the soap film is only a few molecules thick.

Although particles with diameters of 10 to 1,000 Å cannot be seen with an optical microscope, they can be photographed with an electron microscope. The latter employs a beam of electrons rather than a beam of light. The electron beam is focused by magnetic fields, whereas the light beam in the ordinary microscope is focused with glass lenses. The focused electron beam first strikes the material being studied, then strikes a photographic paper and produces a silhouette type of picture.

## COLLOIDAL DISPERSIONS

When a small lump of sugar is placed in water, single molecules break away from the crystal and are scattered among the water molecules. In time the lump disappears, and the resulting mixture is called a solution (Chap. 10). The size of the sugar particles in the solution is essentially that of a single sugar molecule. Because of this particle size, the sugar cannot be removed by filtration, and the

solution appears clear; as a matter of fact, it is as transparent as pure water.

When clay is shaken with water that contains a small amount of sodium hydroxide, the clay breaks up into tiny particles that are scattered among the water molecules. The clay cannot be removed by filtration with ordinary filter paper, nor does it settle on standing. In these respects, the clay-water mixture is like the sugar solution. Unlike the sugar solution, the clay-water mixture is not transparent. This is because the clay does not break up into single molecules; rather, the particles are clusters of clay molecules (ranging in size from approximately 10 to 1,000 Å) that scatter light in random directions. Therefore, the mixture is not properly referred to as a solution. Instead, it is called a **colloidal dispersion** or a **colloidal system**.

It should be pointed out that, when clay and water are shaken together in the absence of a source of  $\text{OH}^-$  ions, most of the clay becomes suspended as particles with diameters larger than 1,000 Å. These particles can be removed by ordinary filtration, and they do settle upon standing. Ordinary muddy water is mostly a suspension of clay in water rather than a colloidal dispersion of clay in water.

We can distinguish between solutions, colloidal dispersions, and suspensions as follows:

solution	colloidal dispersion	suspension
one phase present	two phases present	two phases present
homogeneous	borderline	heterogeneous
does not separate on standing	does not separate on standing	separates on standing
transparent	borderline	not transparent

**Parts of a Colloidal Dispersion.** Colloidal dispersions are composed of two parts: the **dispersed phase**, which consists of the colloidal particles, and the **dispersing phase**, which consists of the continuous matter into which the colloidal particles are scattered. For example, in the clay-water dispersion, the clay is the dispersed phase and the water the dispersing phase.

**Types of Colloidal Systems.** Because both the dispersed and the dispersing phase may be a gas, a liquid, or a solid (except that both may not be gases<sup>1</sup>), there are eight types of colloidal systems. A list of the eight types with examples is given in Table 11-1. The meanings of the terms *foam*, *solid foam*, *liquid aerosol*, *solid aerosol*, *emulsion*, *solid emulsion*, *sol*, and *solid sol* are evident from this table.

<sup>1</sup> Only one phase is present in a mixture of gases.

TABLE 11-1     *Colloidal dispersions*

dispersed phase	dispersing medium	type name	examples
gas	liquid	foam	whipped cream, beer froth, soap suds
gas	solid	solid foam	pumice, marshmallow, polyurethane foam
liquid	gas	liquid aerosol	fog, clouds
liquid	liquid	emulsion	mayonnaise, milk
liquid	solid	solid emulsion	cheese (butter fat dispersed in casein), butter
solid	gas	solid aerosol	smokes, dust
solid	liquid	sol	most paints, starch dispersed in water, jellies
solid	solid	solid sol	many alloys, black diamonds, ruby glass (gold in glass, a supercooled liquid)

**Importance of Colloid Chemistry.** Inasmuch as most substances can exist in the colloidal state, all fields of chemistry are concerned with colloid chemistry in some way or other. All living tissue is colloidal; hence the complex chemical reactions that are necessary to life must be interpreted in terms of colloid chemistry. The portion of the earth's crust that is referred to as tillable soil is composed in part of colloidal material; therefore soil science must include the application of colloid chemistry to soils. In industry, colloid science is important in the manufacture of paints, ceramics, plastics, textiles, photographic paper and films, glues, inks, cements, rubber, leather, salad dressings, butter, cheese and other food products, lubricants, soaps, agricultural sprays and insecticides, detergents, gels and jellies, adhesives, and a host of other products. Such processes as bleaching, deodorizing, tanning, dyeing, and purification and flotation of minerals involve adsorption on the surface of colloidal matter and hence are concerned with colloid chemistry.

Recently a number of products have been marketed that might be described as "instant colloids." A liquid and a gas are confined under pressure in a container; as the mixture is released, the gas expands and forces the liquid out as a foam or an aerosol. Whipped cream and shaving cream are familiar examples of foams; some insect sprays are examples of liquid aerosols. Gases used in forming foams of foods are usually nitrous oxide, carbon dioxide, nitrogen or one of the Freons (the trade name for certain compounds of C, H, Cl, and F). However, it should be noted that in popular usage the term *aerosol* is not necessarily associated with colloids. For instance, a household "aerosol spray" may be merely a gross suspension of liquid droplets in air.

## FORMATION OF COLLOIDAL PARTICLES

Matter can be put into the colloidal state by means of **dispersion methods**, in which large pieces of the substance are broken up into particles of colloidal size, and **condensation methods**, in which mole-

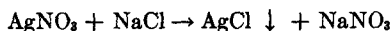
cules or ions or atoms are made to cluster together to form particles of the desired size.

**Dispersion Method of Forming Colloids.** Larger pieces of matter can often be reduced in size by grinding, stirring, beating, or whipping. Specially designed mills called *colloid mills* are used for grinding paint pigments, face powders, and other materials. Beating, stirring, and whipping are employed to form emulsions and foams, such as mayonnaise and whipped cream.

In some cases, larger particles can be made to disintegrate by chemical reagents. As mentioned previously, sodium hydroxide causes clay to break up and become colloiddally dispersed in water. Such a process is called **peptization**, and the reagent that brings it about is called a **peptizing agent**. Certain substances—for example, starch, glue, and gelatin—break up spontaneously into colloidal particles when placed in water. Warming and stirring hasten the process.

**Condensation Method of Forming Colloids.** The formation of fog and clouds by the clustering together of water molecules has already been mentioned. This is an excellent illustration of the condensation method of preparing colloids.

The formation of insoluble substances from solutions is another illustration of this method. If a water solution of silver nitrate is added to aqueous sodium chloride, colloidal silver chloride forms briefly. On standing, the colloidal particles coagulate and form a precipitate:



The process is as follows: In the silver nitrate solution, the silver is present as single ions,  $\text{Ag}^+$ , scattered among the water molecules. The same is true of the chloride ions,  $\text{Cl}^-$ , in the sodium chloride solution. When the two solutions are mixed, silver ions pair off with chloride ions all through the solution to make particles of insoluble silver chloride. Other silver ions and chloride ions bump into the small particles of silver chloride, and the crystals begin to grow. The mixture then takes on a milky appearance because of the formation of colloidal silver chloride. Unless factors that are present prevent further particle growth, the silver chloride particles cluster rapidly together, forming still larger particles that settle to the bottom as a precipitate. Coagulation can be avoided in this case if some gelatin is present to prevent the small silver chloride particles from coalescing. It is logical to assume that, when any insoluble substance precipitates from solution, it passes through the colloidal state.

Colloidal dispersions of metals can be prepared by the arc method. For example, when the ends of two gold wires connected to a source of high-voltage current are brought close together under water (Fig.

11-1), the current sparks across the gap and produces enough heat to vaporize some of the gold. The gold vapor condenses, forming gold particles of colloidal size. The result is a colloidal dispersion of gold in water. This method, known as the *Bredig arc method*, is sometimes classified as a dispersion method, because it first involves the breaking down of larger pieces of matter into atoms.



FIG. 11-1

The arc method of preparing colloids.

Another example of the condensation method of preparing colloids is the process for preparing carbon black, the colloidal form of carbon used as a filler for rubber in automobile tires and in dispersions such as printer's ink and india ink. Carbon black is the soot formed when natural gas is burned in a limited amount of air. Because the carbon is originally present in natural gas mostly in the form of methane,  $\text{CH}_4$ , and because the particle size of gases is the size of the individual molecules, the carbon particles first formed when the hydrogen burns away may be mostly carbon atoms. These aggregate into small particles that collect on cool surfaces from which they are scraped off at suitable intervals.

### STABILITY OF COLLOIDAL DISPERSIONS

When water and an oil, such as gasoline or kerosene, are vigorously shaken together, two unstable colloidal dispersions may result: oil in water and water in oil. The droplets rapidly coalesce into larger droplets that separate into a top oil layer that floats on a bottom water layer (Fig. 11-2). In all *stable* colloidal dispersions, the aggregating of small particles into larger particles must be prevented. This is achieved by one of two methods: **self-stabilization**, or **stabilization by an added component**.

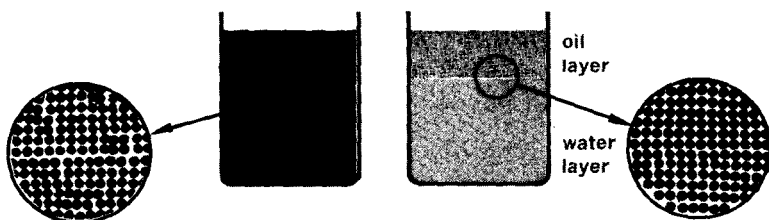
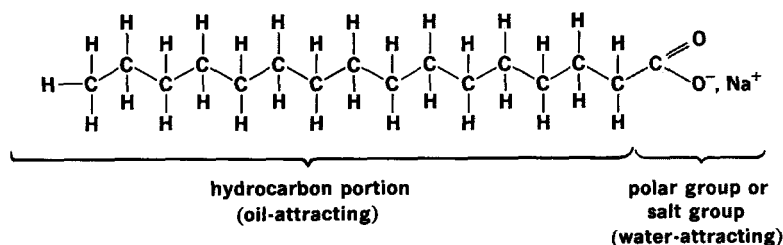


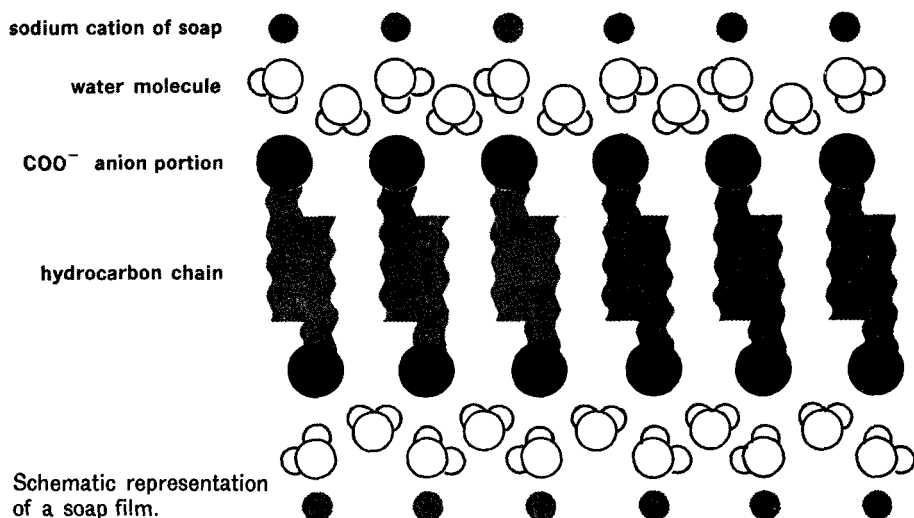
FIG. 11-2

The unstable colloidal dispersion of oil in water (left) rapidly changes to an oil layer floating on a water layer (right).

**Self-stabilization.** Some of the most important colloidal systems form spontaneously and are stable in the same sense that water solutions of salt and sugar are stable. Gelatin, glue, starch, and soap readily form stable colloidal dispersions in water. When these sub-

**FIG. 11-3**

Structural formula of a soap molecule showing the oil- and water-attracting parts.



**FIG. 11-4**

stances are placed in water, there is a tendency for them to dissolve, because the hydroxyl and other polar groups spaced along their carbon-chain molecules tend to form hydrogen bonds with water molecules. These substances do not form true solutions, however, because the hydrocarbon part of their molecules is not attracted by the water molecules (Fig. 11-3). These opposing forces, for and against solution, tend to organize the molecules into particles in which the attractive forces of "like to like" are best satisfied.

Therefore, the particles formed in this regrouping of molecules have the water-attracting portions oriented toward the surface of the particle where they can come in contact with water molecules. The hydrocarbon portion of each molecule is directed toward the interior of the particle where it is mutually attracted to similar portions of other molecules. A cross section of a colloid film composed of soap molecules is shown diagrammatically in Fig. 11-4. In this particle, the hydrocarbon chains are turned inward, and the salt groups (water-attracting) are at the surface of the particle where they are in contact with water.

In self-stabilized particles of the type that we have been discussing, there is a fine balance that involves the attractive forces between unlike molecules (for example, soap-water) and the attractive forces between like molecules (for example, soap-soap and water-water). When the first-named forces sufficiently outweigh the latter, a true solution forms; if the latter sufficiently outweigh the former, the substance does not form a colloidal dispersion spontaneously.

Colloids that are self-stabilizing in water are called **hydrophilic** (water-loving) **colloids**. Glue, starch, gelatin, and soap are examples. However, colloidal dispersions in media other than water are quite common. Therefore, the more general term **lyophilic** (liquid-loving) is used to refer to self-stabilizing dispersions without designating the liquid medium involved. Note that colloidal material that is lyophilic toward one liquid can well be **lyophobic** (liquid-fearing) toward another. For example, starch is lyophilic toward water and lyophobic toward gasoline.

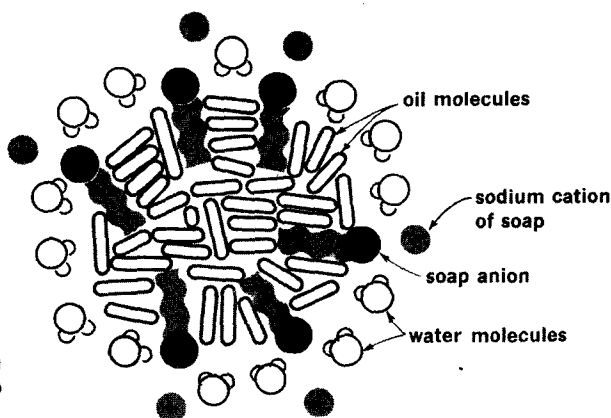
*Stabilization by an Added Component.* In a colloidal dispersion, such as oil in water, where the attractive forces between the same kind of molecules (water-to-water and oil-to-oil) far outweigh the attractive forces of water molecules for oil molecules, the dispersion is stable only if an added component is present that prevents the colloidal particles from coalescing. This type of colloid is called a **hydrophobic** (water-fearing) **colloid**. Water dispersions of mineral oils, or of liquid or solid fats, or of rubber, or of various inorganic substances, such as silver chloride and gold, are examples of dispersions in which the dispersed material consists of a hydrophobic colloid.

The component necessary for the stabilization of hydrophobic colloids may be a protective colloid, or adsorbed ions, or finely divided powders.

**STABILIZATION BY A PROTECTIVE COLLOID.** When oil is shaken with water that contains soap, there results a fairly stable emulsion consisting of oil droplets in the continuous water medium. The soap, a hydrophilic colloid acting as a stabilizing agent for particles of a hydrophobic colloid, is called a **protective colloid**. It is admirably suited for this job because the carbon-chain portion (see Fig. 11-3) is attracted to the oil molecules, and the salt group at the end of the carbon chain is attracted to the water molecules. This results in the formation of a *skin* or *film* (Fig. 11-5) around each droplet of oil, with the carbon chains dissolved in the oil droplet and the salt groups protruding through the surface of the droplet where they touch water molecules.

Soap acts as a protective colloid when it is used to wash dirt and grease off objects. The tiny particles of dirt and grease are coated with the soap and are then attracted by the water and carried away.

A protective colloid must have an attraction for both the dis-



A cross-section diagram of an oil droplet stabilized by soap molecules.

FIG. 11-5

persed phase and the dispersing phase; it must show a preference for one, but not so great as to make it unattracted by the other. These protective films are examples of adsorbed layers.

Gelatin is used as a protective colloid in manufacturing silver bromide dispersions for photographic films and papers. It is also used in making ice cream; here it prevents the formation of large particles of sugar and ice. As it comes from the rubber tree, latex is a milky dispersion of rubber particles in water, with protein material acting as the protective colloid. Agar and gums are other substances that can act as protective colloids in water dispersions of hydrophobic colloids.

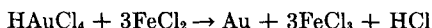
Protective colloids are important in the stabilization of emulsions (colloidal dispersions of two immiscible liquids). In such systems they are called **emulsifying agents**. Milk is an emulsion of globules of butter fat in water, with casein (a protein) serving as the emulsifying agent. Mayonnaise is an emulsion of a liquid fat (such as olive oil or corn oil) in water, with egg yolk playing the role of the emulsifying agent.

**STABILIZATION BY ADSORBED IONS.** Adsorption is a phenomenon in which molecules, atoms, and ions become attached to the surfaces of solids and liquids. Adsorption differs from absorption in that the latter involves penetration by the absorbed material, as when water is absorbed by a sponge. Substances that have been truly adsorbed are not obviously present; adsorbed water on glass, for example, does not give the impression of a damp surface, nor can it be removed with a dry towel.

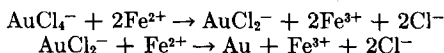
Adsorbed substances are held on surfaces by van der Waals forces or by valence bonds in layers that are usually no more than one or two molecules (or ions) thick. Our discussion is concerned with the adsorption of simple ions by colloidal particles. We shall illustrate this phenomenon with the stabilization of colloidal gold by the adsorption of negative ions. The colloidal gold can be prepared by



the condensation process, a water solution of chlorauric acid being subjected to the action of a reducing agent, such as iron(II) chloride:



The reduction proceeds in a step-wise manner, first forming chloraurous acid,  $\text{HAuCl}_2$ , and then elemental gold:



With single ions originally present in the solution, each particle of gold that first forms during reduction probably consists of a single gold atom. As the gold atoms collide in the mixture, they cluster and form colloidal-sized crystals of gold. The atoms of gold in the surface of these small, irregularly shaped crystals exert strong attractive forces for negative ions, so that  $\text{AuCl}_2^-$  ions are attracted to the surface and held there (by forces of adsorption). Figure 11-6

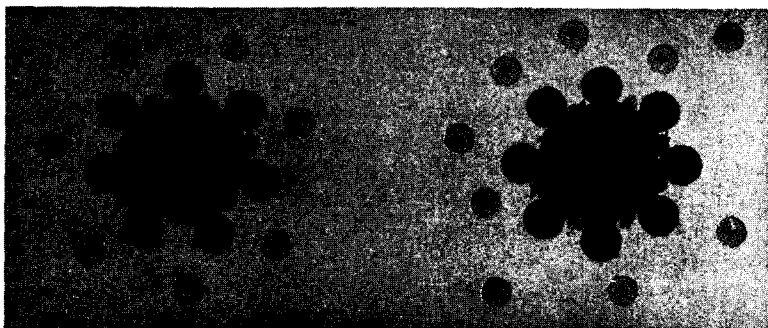


FIG. 11-6

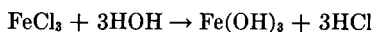
Colloidal gold is stabilized by the adsorption of negative ions.

shows such particles diagrammatically. Because each gold particle becomes negatively charged, owing to the adsorption of negative ions, the gold particles repel one another. This repulsion keeps them from colliding and thus prevents further coagulation, which would precipitate the colloid. Note that the surface of the colloid particle is, in reality, covered by two layers of ions. The first is the layer that we have been discussing—a thin layer, perhaps only one ion thick, of similarly charged ions that are held to the surface by comparatively strong forces. The second layer is more diffuse and ill-defined. It consists mainly of ions which are oppositely charged to those held in the first layer and which are less strongly held by the particle. The ions in the second layer are probably solvated and are free to move about somewhat independently of the colloidal particle. The ions in the first layer determine the charge on the colloidal particle.

Colloidal particles of gold, silver, platinum, and many sulfides acquire negative charges when prepared by precipitation from a water solution (condensation method). Colloidal arsenic trisulfide,

prepared by passing hydrogen sulfide into aqueous arsenic trioxide, is negatively charged by the adsorption of  $\text{HS}^-$  ions. Colloidal silver prepared by the arc process adsorbs  $\text{OH}^-$  ions and is negatively charged.

On the other hand, metallic oxides and hydroxides acquire positive charges. For example, colloidal iron(III) hydroxide<sup>1</sup> particles formed by the following reaction acquire positive charges by the adsorption of either  $\text{H}^+$  or  $\text{Fe}^{3+}$  ions from the solution:



When colloidal particles are similarly charged, regardless of whether all are positive or all are negative, they repel one another and thus resist coagulation.

**STABILIZATION BY POWDERS.** There are many cases in which emulsions are stabilized by fine powders. For example, oil-in-water emulsions are stabilized by clay, lime, calcium carbonate, powdered glass, and pyrites; water-in-oil emulsions are stabilized by carbon.

## PROPERTIES OF COLLOIDAL SYSTEMS

**Tyndall Effect.** All of us have observed the scattering of light by dust particles when a beam of sunlight enters a darkened room through a partly opened door or a slit in a curtain. The dust particles, many of them too small to be seen, look like bright points in the beam of light. If the particles are actually of colloidal size, we do not see the particles themselves; rather we see the light that is scattered by them. This phenomenon, known as the **Tyndall effect**, is due to the fact that small particles scatter light in all directions.

Particles smaller than colloidal size—that is, molecules—also scatter light. However, unless the layer of molecules through which the light passes is quite thick—the sky or a deep lake, for example—the effect is not apparent to our eye.

The Tyndall effect can be used to differentiate between a colloidal dispersion and a true solution, because the atoms, molecules, or ions that are present in a solution do not scatter light noticeably (Fig. 11-7). This scattering of light accounts for the opacity of colloidal dispersions. For example, although both olive oil and water are transparent, a colloidal dispersion of the two has a milky appearance.

The blue of the sky is due to the fact that the small particles, including molecules of nitrogen and oxygen, scatter the shorter wavelengths (blue) more effectively than the longer wavelengths. If it were not for this scattering, light would reach us only by direct transmission from the sun or by reflection from surfaces; hence the

<sup>1</sup> The composition of colloidal iron(III) hydroxide is probably better represented by  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  than by  $\text{Fe}(\text{OH})_3$ .



The Tyndall effect. The bottle on the left contains a fairly concentrated solution of copper sulfate in water. The other bottle contains a colloidal dispersion made by adding a single drop of India ink to water. The path of the beam of light from the spotlight at the left is hardly visible in the true solution but shows brightly in the colloidal dispersion.

FIG. 11-7

sky would appear as dark in daytime as at night, with the sun acting as a huge spotlight during the day.

**Brownian Movement.** The ultramicroscope (Fig. 11-8) is a device for viewing the Tyndall effect through an optical microscope. The optical microscope is focused on the colloidal dispersion at right angles to the light source and with the background in darkness.



FIG. 11-8

Under these conditions, the particles are observable not as particles with definite outlines, but as small, sparkling specks.

One remarkable feature of the ultramicroscope is that it enables us to see that the dispersed colloidal particles are constantly moving in random, zigzag paths (Fig. 11-9). This erratic motion is accounted



FIG. 11-9

Brownian movement. A plot of the observed position of a colloidal particle every 30 sec. (From Jean Perrin, *Les Atomes*, Presses Universitaires de France, 1948, p. 112.)

for on the assumption that the molecules of the dispersing medium are constantly colliding with the colloidal particles and imparting motion to them. This random motion of colloidal particles in a dispersing medium is called **Brownian movement**, after the British botanist Robert Brown, who first observed it in 1827 in a suspension. This movement is strong evidence in support of the kinetic molecular theory, which postulates that molecules are in constant motion. We cannot observe the motion of water molecules, but we can observe its effect on small particles of colloidal matter suspended in the water.

**Rate of Settling.** One of the striking characteristics of colloidal systems is the fact that very dense dispersed particles do not sink but may remain suspended indefinitely in a dispersing medium of much

lower density. Gold sols in water can be quite stable; the carbon-water colloid shown at the right in Fig. 11-7 has not noticeably changed for more than fifteen years. In this respect, dispersed colloidal particles are like simple molecules in a solution. Both have rotational and translational kinetic energies (called Brownian movement for colloidal particles) and both tend to diffuse throughout a medium. However, even molecules tend to settle in a gravitational field, although this settling is not perceptible in a small container where the vertical column is short. This settling is dependent on the gravitational force acting on the particle, the difference in the density of the particle and of the suspending medium, the viscosity<sup>1</sup> of the medium, and the size of the particle. Because the velocity of settling is proportional to the square of the radius, the time required for sedimentation increases rapidly with decreasing particle size. It has been calculated that a silver sphere of radius  $1 \times 10^{-3}$  cm would require 5 sec to settle a distance of 1 cm in water, whereas a silver sphere of radius  $1 \times 10^{-6}$  cm would require 5,000,000 sec (58 days) to settle the same amount. Convection currents would probably be sufficient to keep such colloidal matter suspended indefinitely in spite of this slight tendency to settle.

**DETERMINATION OF AVOGADRO'S NUMBER AND MOLECULAR WEIGHTS.** Gaseous molecules in a container in a uniform gravitational field tend to settle. The random motion of the molecules tends to counter the settling process and to scatter the molecules uniformly throughout the container. As usually happens when we are dealing with a system in which two opposing forces are in operation, the system comes to equilibrium if conditions are kept constant. In the case of gases, the equilibrium condition represents a compromise between complete sedimentation and complete random distribution of the molecules throughout the container. That is, the number of molecules in a unit of volume increases at lower levels in the container, but molecules are always present at the top of the container, and the gradation in concentration from top to bottom remains constant at equilibrium. The difference in concentration of gaseous molecules with height is negligible in ordinary containers; however, the difference is quite noticeable in the atmosphere, where the "container" has a very great height.

The German physicist Ludwig Boltzmann, in 1890, derived a mathematical expression that describes the distribution of energy among gaseous molecules at equilibrium in a uniform gravitational field. Another form of the Boltzmann relationship describes how the concentration of molecules increases from top to bottom in the gravitational field. The Boltzmann equation can be modified in a number of ways by the substitution of appropriate terms. One useful modification contains the Avogadro number as one of its

<sup>1</sup> The viscosity of a liquid is a measure of its resistance to flow. Molasses and tar have high viscosities, whereas water and gasoline have low viscosities.

terms,<sup>1</sup> and it is with this modification that we are concerned in the experimental determination of the Avogadro number as described below.

Early in this century (1908), the French scientist Jean Perrin realized that he could develop an experimental method for determining Avogadro's number, provided dispersed colloidal particles behaved as did gaseous molecules, that is, provided the colloidal particles varied in concentration in a container from top to bottom according to the Boltzmann relationship. Perrin was able to count the number of colloidal particles at various levels by means of the ultramicroscope. He then substituted his data in the Boltzmann equation and calculated a value for the Avogadro number. His values, reported in 1908 as  $6.0 \times 10^{23}$  and  $5.4 \times 10^{23}$ , agreed rather well with those obtained by other methods.

Molecular weights of "giant molecules" that compose viruses, proteins, plastics, etc., are usually determined by measuring the sedimentation characteristics in gravitational fields hundreds of times larger than the earth's field. These huge gravitational fields are obtained by whirling a dispersion in high-speed centrifuges. Frequently, some information about the shape of the molecule can also be obtained from the rate of sedimentation.

**Electrophoresis.** The charged, dispersed particles in a colloidal system moves toward the electrode that has the opposite charge. This movement is called **electrophoresis**. By putting two electrodes into a colloidal system and connecting them to a source of direct current, we can determine (1) if the particles are charged and (2) whether the charge is positive or negative (Fig. 11-10).

If the colloid particles reach the electrode, they are neutralized, and the colloidal system is precipitated. The dispersed phase usually coagulates and precipitates below the electrode, although in some cases it may be deposited on the electrode in a manner that resembles the electroplating of metal.

Electrophoresis is of importance commercially. For example, natural or synthetic rubber can be electrodeposited on anodes of various shapes. Thus an anode shaped like a hand is used in making rubber gloves. Many types of rubber articles are made in this way.

<sup>1</sup> Avogadro number =  $\frac{RT}{[(d_c - d_m) V g (H_2 - H_1)]} \ln N_1 / N_2$  where  $R$  is the gas constant,  $T$  is the temperature in °K,  $N_1$  and  $N_2$  are the number of colloidal particles at height  $H_1$  and  $H_2$ , respectively, and  $d_c$  and  $d_m$  are the densities of the colloidal particle and the dispersing medium,  $V$  is the volume of a colloid particle,  $g$  is the acceleration due to gravity, and  $\ln$  is the natural logarithm (see page 423). Perrin had to count and weigh the colloidal particles in order to get the volume  $V$  of one particle,  $V = \text{weight}/(\text{density} \times \text{number})$ . Having values for all the terms on the right, Perrin used the equation above to calculate the Avogadro number. Because the Avogadro number is now well established and because the mass of one particle is equal to  $d \times V$  the relationship above may be further modified to give an expression for calculating the weight of one mole and hence the molecular weight. The method is applicable only to very large molecules.

Electrophoresis of red gold sol. The colloidal gold (small spheres) is displaced toward the positive pole, showing that the gold particles are negatively charged.

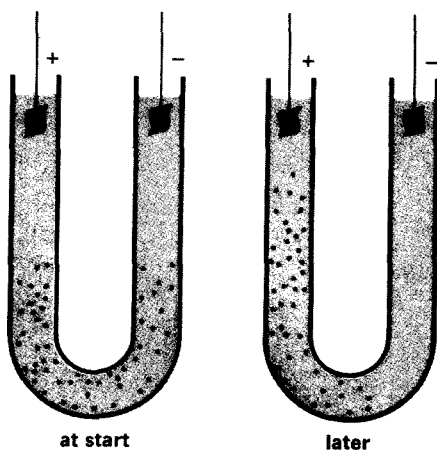


FIG. 11-10

A cube 1 cm on each edge has a surface area of  $6 \text{ cm}^2$ . If this cube is subdivided into 1000 cubes and each of these in turn is subdivided into 1000 cubes ( $0.01 \text{ cm}$  on an edge), the surface area will be  $600 \text{ cm}^2$ . If the cubes are further subdivided into cubes  $1 \times 10^{-7} \text{ cm}$  on an edge, the amount of surface will be  $60,000,000 \text{ cm}^2$ .

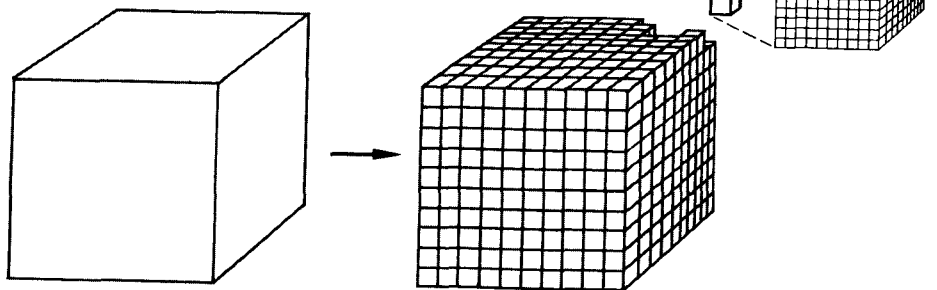


FIG. 11-11

The process is also important in biochemical research. Colloids present in organic materials, for example, proteins and related substances, may be separated and identified by electrophoresis.

**Adsorption.** Matter in the colloidal state has a tremendous amount of surface. To emphasize the point, let us consider a cube of iron that is  $1 \text{ cm}$  on an edge (Fig. 11-11). Such a cube would weigh  $7.86 \text{ g}$  (about  $0.25 \text{ ounce}$ ) and have a surface of  $6 \text{ cm}^2$ . If this cube is subdivided into a thousand billion billion small cubes, each of these cubes will be  $1 \times 10^{-7} \text{ cm}$  ( $10 \text{ \AA}$ ) on an edge and hence will be a colloidal particle. The amount of surface of the  $7.86 \text{ g}$  of iron now is not  $6 \text{ cm}^2$  but  $60,000,000 \text{ cm}^2$ —about  $1.5 \text{ acres}$ . Considering the large amount of surface, it is not surprising that the most important properties of colloidal matter are those which are dependent on surface interactions such as adsorption.

The huge surface area of colloidal matter makes it particularly efficient in attracting and holding molecules, atoms, and ions of other substances. This phenomenon (adsorption) has already been discussed briefly in connection with the stabilization of colloidal particles. Because a given colloid shows a preference in what it adsorbs, the process of adsorption is widely used in the removal of undesirable colors and odors from certain materials, for the separation of mixtures, for the concentration of ores, and in various other purification processes. Space permits mentioning only a few examples of the commercial application of this phenomenon.

For use in war and riots, gas masks have been devised that contain activated charcoal or some other type of adsorbent. Activated charcoal is made by heating charcoal in air or steam so that more than half of the carbon is burned away. This leaves a very porous carbon "skeleton" of the original piece of wood, so porous that a very large percentage of the remaining carbon atoms are exposed and hence capable of adsorbing. In addition to its present use in commercial gas masks, activated charcoal is widely used in industry and in laboratory work to remove impurities that have objectionable odors, flavors, colors, etc. It is also used in some cigarette filters, presumably with the aim of removing carcinogenic compounds from tobacco smoke.

Raw sugar as it is first obtained from sugar cane juice has a dark brown color due to the presence of plant pigments. These pigments are removed by dissolving the sugar in warm water and then passing the solution first through beds of diatomaceous earth (a porous, finely divided mineral) and then through beds of granular boneblack (charcoal made by the destructive distillation of bones). These materials adsorb the colored compounds so that the sugar solution is

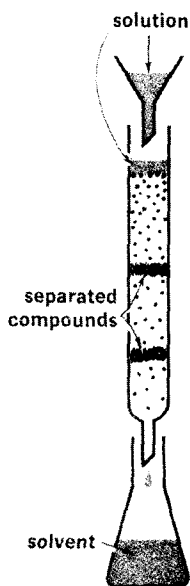


FIG. 11-12

#### Column chromatography.

colorless. The water is then evaporated, yielding pure table sugar.

The separation of trace materials from mixtures—for example, the separation of vitamins and hormones from biological samples—presents an exceedingly difficult problem. Much success has been achieved by taking advantage of the difference in the tendency of the components of a mixture to be adsorbed on certain powdered materials. This method, called **chromatographic separation** or **chromatography**, employs a column of a solid, such as starch, aluminum oxide, sugar, etc. (Fig. 11-12). A solution of the mixture is allowed to seep downward through the column. The component most strongly adsorbed is held close to the top of the column, the component next most strongly adsorbed is held just below the first component, and so on down the column. If the adsorbed materials are colored, bands of color will denote the location of each component. Frequently, the location of colorless adsorbed material is

## Paper chromatography.

determined by testing for fluorescent bands with ultraviolet light. The adsorbed material is removed by pouring quantities of fresh solvent down through the column. The component least readily adsorbed is dissolved from the column first.

An important modification of the chromatographic method makes use of specially prepared cellulose paper. In **paper chromatography** a drop of the solution of the compounds to be separated is placed on a strip of paper. Initially, the solute tends to become adsorbed at one spot on the fibers of the paper. If fresh solvent is allowed to spread through the paper, the solute compounds are carried along, being continuously adsorbed and redissolved. Compounds that are strongly adsorbed tend to lag behind; compounds weakly adsorbed are carried along more rapidly by the advancing solvent. The solute compounds tend to become separated, held at different spots by the cellulose fibers (Fig. 11-13). The paper can finally be cut into pieces, and each piece extracted with a solvent to obtain the solutes separately.

Not only are different solute compounds adsorbed on paper more or less tenaciously, but solvents also vary greatly in their attraction for cellulose fibers. A solvent that is adsorbed strongly tends to displace adsorbed solutes and move them along efficiently from one site of adsorption to the next. A demonstration of the great difference in attraction for cellulose between water and carbon tetrachloride is shown in Fig. 11-14.

**Gas chromatography** employs the gas phase as carrier for adsorbates instead of the liquid phase. It is especially valuable in separating and purifying small amounts of gases or liquids, amounts too small to handle by ordinary distillation methods. Mixtures of gases or vaporized liquids are passed through an adsorbing column (at a temperature above the condensation point of any liquid present). Some carrier gas, such as helium, is used to move the vapors through the column. Thus, the method is comparable with the method discussed in the previous paragraphs, except that in the former a liquid solution passes through the column, and a liquid solvent is used to move the adsorbed compounds through the column. In gas chromatography a gaseous mixture passes through, and a gas is used to move the adsorbed material from one section of the column to the next as the compounds become separated. An important feature is that the movement of various compounds through the column can

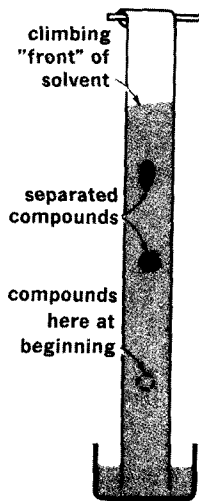


FIG. 11-13



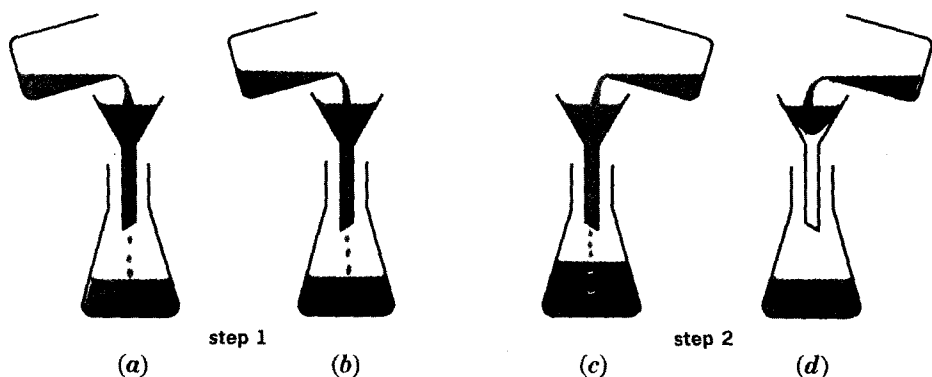


FIG. 11-14

An illustration of the relative attractive forces between cellulose-carbon tetrachloride and cellulose-water. (a) Carbon tetrachloride readily passes through filter paper; (b) Water readily passes through filter paper; (c) Water passes through the filter paper used in the filtration of carbon tetrachloride (and still wet with carbon tetrachloride); (d) Carbon tetrachloride does not pass through the filter paper used in the filtration of water (and still wet with water).

be followed by automatic devices that measure and record the heat conductivity of gaseous mixtures as they flow past a sensitive detector. Because the heat conductivities of various gases differ greatly, the presence of a second gas mixed with the carrier gas is easily detected. An abrupt change in heat conductivity is noted when a second gas begins to pass the detector with the carrier gas; when all the second gas has moved past the detector and only the carrier gas is present, a compensating abrupt change in heat conductivity is noted (see Fig. 11-15). Commonly a heat-conductivity detector is put at the end of a chromatographic column; as different samples of the separated gases come off the column, they can be collected in individual containers if desired.

Another field in which adsorption is extremely important is catalysis. The speed of many chemical reactions is increased when they are carried out in contact with a solid colloidal material. Finely divided nickel is much used as a catalyst for the hydrogenation of liquid fats to solid fats, and colloidal platinum is an excellent catalyst for the oxidation of sulfur dioxide to sulfur trioxide in the manufacture of sulfuric acid. There is considerable evidence that such reactions often occur while one of the reactants is adsorbed on the surface of the catalyst (see Chap. 12).

*Color of Colloidal Systems.* The color of a common dye or pigment is due to the selective absorption of wavelengths from white light by the dye. This absorption is dependent on the structure of the molecules of the dye.

Color can also be produced by the selective scattering of white light by colloidal material. The particular wavelengths that are most

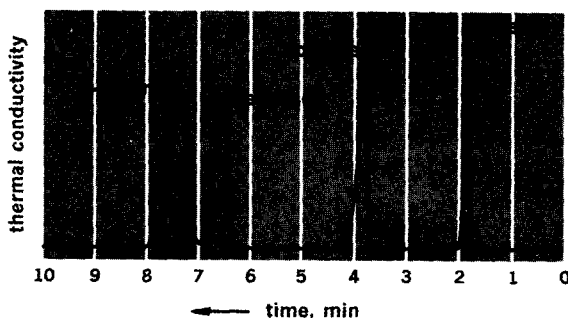


FIG. 11-15

A gas chromatograph showing the separation of a mixture containing 0.004 ml of ether, 0.007 ml of acetone, 0.009 ml of benzene, and 0.012 ml of 2-butanol. Note that all of the ether came through the column within 2 min after the mixture had been added. Acetone came through about 2 min later, then benzene, and finally butyl alcohol, the entire process requiring 8 min. Area under a peak is a measure of the relative amount of the substance causing the peak. (Courtesy of Dr. N. S. Bowman, University of Tennessee.)

efficiently scattered are determined by the size and shape of the particles. Gold sols have been obtained in several shades of red, blue, and violet, depending on the size of the dispersed gold particles; silver sols can be made in different shades of red, green, blue, gray, and black.

The particles in tobacco smoke and skim milk scatter the shorter wavelengths, so that these colloidal dispersions appear blue in reflected light and red in transmitted light. The blue eye color is due not to pigment, but rather to the scattering of light by colloidal material in the iris. Different shades of blue are accounted for by the particle size of this material; larger particles make the eyes gray. Other colors, for example, green, brown, black, are accounted for by a combination of two factors: the scattering of light in the blue region and the presence of a yellowish-brown pigment in front of the iris that causes selective absorption of light.

## COAGULATION OF COLLOIDAL DISPERSIONS

It is often desirable during chemical operations to coagulate colloidal dispersions. Industrial smokes and dusts, colloidal precipitates in laboratory work, and foam formation during distillations are examples of colloidal dispersions that we generally desire to coagulate. Also, we frequently wish to coagulate natural sols and emulsions to obtain valuable products. Such products include butter and cheese from milk, and rubber from the sap of the rubber tree.

There are several methods of bringing about the coagulation of colloidal dispersions. In many cases, heating is all that is necessary. The protein colloid in an egg is coagulated by heating for a few

minutes. In laboratory work, a mixture that contains a precipitate is often held at an elevated temperature for a short time before filtering in order to coagulate the fine particles.

Perhaps the most effective way of coagulating colloidal dispersions of the sol and emulsion type is by adding an electrolyte. This introduces a very large number of ions that remove the adsorbed ions, so that the colloidal particles no longer repel one another but coalesce rapidly into larger particles. The choice of electrolyte is dependent on the type of adsorbed ions to be removed. For colloidal gold, because the adsorbed ions are negative ions, the most effective coagulating electrolytes are those which have positive ions of high charge. For this reason, aluminum chloride ( $\text{Al}^{3+}$ ,  $3\text{Cl}^-$ ) is more effective than an equivalent quantity of sodium chloride ( $\text{Na}^+$ ,  $\text{Cl}^-$ ) or calcium chloride ( $\text{Ca}^{2+}$ ,  $2\text{Cl}^-$ ) in coagulating gold sols. On the other hand, colloidal ferric hydroxide (positively charged) is more effectively coagulated by sodium sulfate ( $2\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ) than by an equivalent quantity of sodium chloride ( $\text{Na}^+$ ,  $\text{Cl}^-$ ).

Hydrophilic colloids, and colloids protected by adsorbed films of hydrophilic colloids, are also coagulated by electrolytes. This is because these colloids—gelatin and other proteins, soaps, starch, and glue—have polar groups that are strongly affected by a high concentration of ions. Raw rubber is obtained by adding acetic acid to the sap from rubber trees. The time-honored method of obtaining butter from milk is to let the milk sour (the dissolved sugar ferments, forming lactic acid). The acid thus formed is effective in removing the protective colloid casein, so that the butter fat globules can cluster together and form larger fat particles.

The mixing of two colloidal dispersions whose particles are oppositely charged causes both to coagulate.

A commonly used procedure for destroying smoke and other types of aerosols is the Cottrell method of electrical coagulation. The smoke is led past a series of sharp points charged to a high potential (20,000 to 75,000 volts). The points discharge and form ions in the air. Smoke particles adsorb these ions and become so highly charged that they are attracted to and held on the oppositely charged electrodes.

"Rain making" has been achieved, but not on a practical scale, by seeding clouds with solid carbon dioxide or with silver iodide crystals. Recently, airport fogs have been successfully dispelled by seeding them with dry ice.

*Dialysis.* Because the presence of excess ions gradually brings about the coagulation of colloids, the removal of some ions is necessary if the dispersion is to be kept for any length of time. Colloidal gold prepared by the reduction of gold chloride soon coagulates, unless most of the  $\text{Fe}^{3+}$  and  $\text{Cl}^-$  ions are removed. This can be done by placing the colloidal dispersion in a container, the bottom of

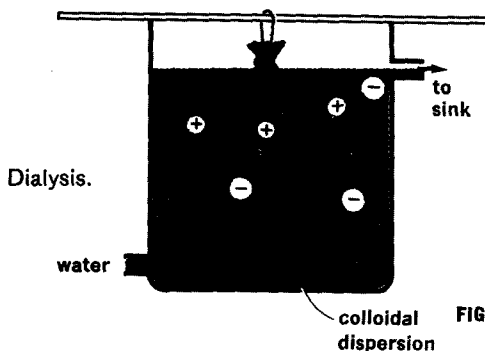


FIG. 11-16

which is made of a semipermeable membrane, that is, permeable to ions and water molecules but not to the larger colloidal particles. The container is then placed in circulating distilled water (Fig. 11-16). The ions diffuse through the membrane and are carried away in the water. Animal membranes, cellophane, and parchment paper are suitable for the membrane. The separation of ions from colloids by diffusion through a semipermeable membrane is called **dialysis**.

## GELS AND JELLIES

The word **gel** is a general term that includes all such solid and semi-solid colloids as jellies, gelatinous precipitates, membranes, synthetic and natural fibers, and similar materials.

The type of gel that is commonly referred to as a **jelly** (fruit jellies, Jell-O, jellied alcohol) belongs to the **sol** type of colloidal dispersion, that is, a solid dispersed in a liquid. These systems appear to be more or less solid, even though the dispersed solid phase often makes up less than 1 per cent of the total. The semisolid structure of jellies is accounted for on the assumption that molecules of the colloidal material aggregate into long, filamentlike structures. These

Electron micrograph of sodium soap fibers in a lubricating grease. Oil is held in the tangled brush-heap structure of the soap. (Courtesy of Dr. A. M. Cravath, Shell Development Company.)



elongated particles become entangled, forming a "brush-heap" structure that is capable of retaining large amounts of liquid, so that the whole appears to be a solid (Fig. 11-17). In fruit jellies, the carbohydrate *pectin* is responsible for forming the brush-heap struc-

FIG. 11-17

ture. It is now common practice to use commercial preparations of pectin (Certo, Sure-Gel), for the amount of jelly and jam obtained from a given amount of fruit is considerably increased by their use. The entrapped water contains dissolved sugar, organic acids, and other substances.

One of the most effective incendiary bombs used in World War II contained a jellied petroleum oil, an aluminum soap serving as the brush-heap structure. Alcohol can be jellied with calcium acetate or with cellulose esters. "Canned heat" is a gel of alcohol and a cellulose ester.

## CHAPTER REVIEW

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### *Terms*

Colloidal state, dispersed phase, dispersing phase, foam, sol, emulsion, aerosol, dispersion method, condensation method, peptization, stabilization, hydro- and lyophilic, hydro- and lyophobic, protective colloid, Tyndall effect, Brownian movement, ultramicroscope, viscosity, electrophoresis, adsorption, chromatography, Cottrell method, dialysis, gel, jelly.

### *Exercises*

1. Taking 1,000 Å as the diameter of a rather large spherical colloidal particle, estimate the atomic diameters from Fig. 4-15 of carbon, aluminum, and cesium, and calculate the appropriate number of atoms of each in large colloidal particles. Assume each atom occupies a space equal in volume to the cube of its diameter.
2. Could a piece of cotton fluff the size of a hen's egg possibly be considered to be in the colloidal state? Explain.
3. Colloidal sols cannot be separated by filtration through ordinary filter paper. What does this tell one about the paper?
4. Describe an experimental method for determining whether a given liquid that appears clear is a true solution, a colloidal dispersion, or a single pure compound.
5. In gravimetric methods of analysis a solid precipitate is formed, filtered, dried, and weighed. Barium sulfate is a typical "insoluble" substance that can be so treated, being formed when a solution containing  $\text{Ba}^{2+}$  ions reacts with one containing  $\text{SO}_4^{2-}$  ions. If filtration is attempted immediately after precipitation, the solid barium sulfate goes through the filter, but if the precipitate is allowed to stand for some time, it can be caught on the filter. Gentle heating of the mixture of solid and solution decreases the time needed to form a filterable precipitate. Suggest an explanation for the differences in filterability.

6. Butter is described as a colloidal dispersion, but solid paraffin wax is not. Suggest how their structures may differ.
7. Certain so-called fluffy solid kitchen fats might be described as one of the housewife's most expensive supplies of air. What type of colloidal dispersions might these be?
8. Compare the terms solute and solvent with dispersed and dispersing phases. Of what do the dispersed and dispersing phases consist in each of the following: a gold sol, fog, whipped cream, smoke, mayonnaise, ruby glass?
9.
  - a. By means of a diagram, show how an aerosol dispenser of whipped cream or shaving cream probably operates.
  - b. Usually, an aerosol dispenser has a label warning against disposing of it by burning, even when it is empty. Explain.
10. Slightly acidic muddy pond water becomes clear on standing more quickly than slightly basic water. Why?
11. Untreated cotton garments take a much longer time to dry after washing than the "drip-dry" fabrics. Suggest an explanation of this difference based on possible molecular structures.
12. Certain fabrics, for example, cotton, can be waterproofed by coating them with appropriate substances. Describe in hypothetical terms, using a diagram, one type of waterproofing substance, hopefully a long-wearing one.
13. Suggest a way of causing two immiscible liquids to form a fairly stable heterogeneous mixture.
14. Which of the following electrolytes is most effective in coagulating a gold sol:  $\text{FeCl}_3$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{Na}_2\text{SO}_4$ , or  $\text{K}_3\text{PO}_4$ ? Why? Which one is most effective in coagulating an iron(III) hydroxide sol? Why?
15. It is mentioned that gelatin is used in the manufacture of silver bromide for photographic film. What part does the gelatin play?
16. Describe two experimental methods that could be used to determine the charge on the colloidal particles of a given sol.
17.
  - a. How is the time of settling of a particle in a medium, say water, related to the diameter of the particle?
  - b. Explain, using a diagram, why colloidal particles in water, despite an appreciable theoretical rate of settling, nevertheless may remain suspended practically indefinitely.
18. Certain types of freshly prepared colloidal dispersions are not stable unless dialyzed. Suggest some that might fall in this category, and then explain why dialysis increases the stability of the dispersion.
19. "The behavior of colloidal particles in sols provides a good model of the behavior of gas particles." Is this statement justifiable or not? Explain fully.
20. Cite several examples of the use of emulsifying agents in the preparation of foods and of commercial products.

21. If the dispersing phase is a liquid and the dispersed phase is in the form of single molecules, we usually call such a mixture a solution, although it could be a colloid. Explain.
22. Suggest explanations for the following:
  - a. Two stable sols on being mixed soon precipitate one another, leaving a true solution.
  - b. Two stable sols on being mixed form a stable mixture of sols.
  - c. Gold is over nineteen times as dense as water; yet colloidal gold does not sink noticeably in water.
  - d. A curd is formed when milk is poured on sour fruit.
  - e. Soap is effective in removing grease.
  - f. Apple juice forms a jelly when sufficiently concentrated.
  - g. Colloidal material carried in rivers precipitates and forms deltas when the river water flows into the ocean.
  - h. If gasoline is poured through a filter paper and followed by water, the water passes through easily; but if water is first poured through the paper, gasoline does not then run through it.
  - i. A brownish water solution poured through a bed of charcoal emerges as a colorless liquid; then colorless acetone is poured through the same bed and emerges as a brownish liquid.
23. Explain how a rare vitamin might be obtained from plant juices by the chromatographic process.
24.
  - a. Calculate the size in cubic angstroms of a cubic particle of iron that has an edge approximately equal in length to the shortest wavelength of visible light.
  - b. Assuming, for ease of calculation, that the atoms are packed as little cubes, how many iron atoms would there be in the particle?
  - c. Is such a particle in the size range of colloidal particles?
25. The farmer adds water-soluble compounds ( $\text{KNO}_3$ ,  $\text{NH}_4\text{NO}_3$ , etc.) to his soil as plant foods. Why does not the first hard rain remove them all from the soil?
26. Some fruit juices, for example, apple juice, have a greater tendency to jell than others, for example, grape juice. Can you give a possible reason for this?
27. By means of a labeled diagram show how a gas mask might work. List some possible peacetime uses for such masks.
28. Calculate the surface area in square centimeters of 1.0 g of iron in the form of particles of the size described in Exercise 24a.
29. A small amount of liquid *A* is shaken violently with water. Describe the relative forces existing between the various molecules if (a) a solution forms, (b) a stable colloidal dispersion forms, or (c) an unstable suspension forms.
30. A piece of cloth, for example, a handkerchief, if dried thoroughly, say in a desiccator over phosphorus(V) oxide, becomes warm to the touch when it is allowed to come in contact with ordinary air. Suggest a reason for this and discuss the energy relationship involved.

31. Describe how a mixture of the gases  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  might be separated by gas chromatography.
32. It has been found that by spraying powdered dry ice a cold, low lying fog on and over airport runways can sometimes be dispersed. It is reported that the fog usually clears within half an hour after treatment. Suggest a possible mechanism for the changes involved.
33. How are dialysis and osmosis alike? How are they unlike?

### SUPPLEMENTARY READING

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## REACTION RATES;

## CHEMICAL

## EQUILIBRIA



Chemical and physical equilibria have already been discussed briefly. A saturated sugar solution containing undissolved sugar was cited in Chap. 10 as an example of a physical equilibrium. In this system, undissolved sugar molecules are in equilibrium with dissolved sugar molecules. If kept in a closed container at constant temperature, undissolved sugar molecules continue to break away from the crystal structure and pass into solution. The reverse process also takes place; that is, dissolved sugar molecules leave the solution and join the crystal. Because these opposing changes are occurring at the same rate, there is no change in the concentration of the sugar solution, and the system appears to be at rest. During a long period of time, weeks or months, the shape of the solid sugar crystals will change, but the total weight of solid sugar remains the same. Actually, the rate of dissolving will remain equal to the rate of crystallization so long as no external change is made that affects the system. This is an example of a *dynamic equilibrium system*, rather than a static system.

### REVERSIBLE REACTIONS AND CHEMICAL EQUILIBRIA

When the products of a specific chemical change can react to form the original substances, the change is said to be **reversible**. The pair of reactions, the forward and the reverse reaction, are referred to as *two opposing chemical changes*. In chemical reactions that are reversible, a condition of chemical equilibrium results if conditions permit the opposing reactions to occur at the same rate. The following discussion is concerned with opposing chemical changes, reversible reactions, and the establishment of a chemical equilibrium.

Consider the union of hydrogen and nitrogen to form ammonia—Eq. (1)—and the reverse or opposing reaction, the decomposition of ammonia to form hydrogen and nitrogen—Eq. (2):



When hydrogen and nitrogen are mixed in a 3:1 ratio by volume at room temperature, a reaction does not occur at a detectable speed; however, at elevated temperatures, in the presence of a catalyst, the reaction is rapid. At a temperature of 200°C and a pressure of 30 atm, this mixture reacts rapidly till about 67.6 per cent of the pressure exerted by the mixture is due to ammonia gas. No further apparent change occurs in the amounts of the three components present so long as the mixture is held at 200°C and 30 atm.

Similarly, ammonia does not decompose at room temperature—Eq. (2)—at a detectable rate. But, in the presence of a catalyst, if the temperature of the ammonia is raised to 200°C and the pressure is raised to 30 atm, its decomposition into hydrogen and nitrogen occurs at a measurable speed. The amount of ammonia diminishes till 32.4 per cent of the pressure exerted by the mixture is due to hydrogen plus nitrogen; after this there is no further apparent change.

Regardless of whether we start with pure ammonia or with pure hydrogen and nitrogen, neither reaction goes to completion; each appears to end by forming a mixture that contains in terms of pressure exerted:

67.6 per cent ammonia

32.4 per cent hydrogen and nitrogen

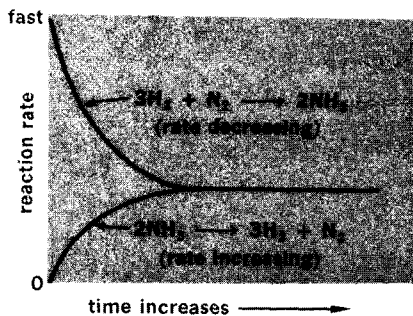
The percentage in terms of pressure is the same as the percentage in terms of volume.

Here we are dealing with two opposing reactions, each of which takes place in such a way that the other can occur at the same time, once the reaction has been started.

If we start with only hydrogen and nitrogen in the container, reaction (2) cannot at first occur because there is no ammonia. However, as reaction (1) proceeds, ammonia forms, and reaction (2) starts, at a low rate initially because not much ammonia is present. Reaction (1) may be occurring at a very rapid rate. As time goes on, the speed of reaction (1) steadily decreases, because hydrogen and nitrogen are being used up, and the speed of reaction (2) steadily increases, because the amount of ammonia is increasing. Eventually the speeds of the two opposing reactions become equal (Fig. 12-1). Once the reaction rates equalize, the amounts of hydrogen, nitrogen, and ammonia do not change so long as the temperature and pressure do not change and nothing is added to or removed from the container. Both reactions continue, and the system is in a state of dynamic equilibrium.

When we start with ammonia in a closed container at 200°C and 30 atm, the same reactions occur, but in the reverse order.

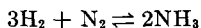
## REACTION RATES; CHEMICAL EQUILIBRIA



A graph showing how the reaction rates for the synthesis and decomposition of ammonia change with time. Initially, only hydrogen and nitrogen are present.

FIG. 12-1

A **chemical equilibrium** is a system in which two opposing reactions are proceeding at the same rate. The equilibrium state is indicated by double arrows, as shown in the following equation:



It should be noted at this point that the relative amounts of reactants and products present at equilibrium may vary greatly. The amounts at equilibrium depend on the substances that are reacting, the temperature, and the concentrations at the beginning of the reaction. These factors are discussed in detail in subsequent sections.

*Importance of Chemical Equilibria.* Because most chemical reactions can come to a state of equilibrium under the conditions necessary to start the reaction, an understanding of how to avoid or how to establish an equilibrium is very important. The chemist or chemical engineer who is concerned with the large-scale manufacture of a useful compound is most interested in minimizing the influence of the reverse reaction. In a living organism there are many chemical equilibrium processes that are responsible for the well-being of the organism. For example, the acidity (or alkalinity) of the blood is maintained within very narrow limits by several opposing chemical reactions. Hence the research doctor, the pharmacologist, the nutritionist, the biochemist, and the soil chemist constantly study equilibrium processes in their efforts to solve the problems involved in making plants and animals healthier. The research chemist must delve deeply indeed into this important subject.

## RATE OF REACTION

By the **rate** or **speed of a reaction** is meant the amount of reactants converted to products in a unit of time. The amount of reactants is usually expressed in moles per liter; the unit of time may be a second, a minute, an hour, or a day, depending on whether the reaction is fast or slow.

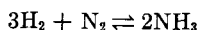
Methods for determining the amount of products vary according to the nature of the reaction. If a gas is one of the products, its volume

can be determined from time to time. If the reaction is being carried out in solution, samples can be taken at suitable intervals for analysis. When ordinary analytical methods are employed, it is difficult to measure the reaction rate for a rapid reaction, because the reaction may be over before even one analysis can be performed. However, by means of specialized instruments chemists have been able to estimate the rates of detonations of explosives and of even such apparently instantaneous reactions as the neutralization of an acid with a base, for example, HCl with NaOH.

Inasmuch as an equilibrium results when the rates of two opposing reactions become equal, we shall begin the discussion of chemical equilibria by considering the four factors that influence reaction rates. First, we shall take up each of the three influences: nature of the reactants, temperature, and concentration. We then develop the idea of the equilibrium constant, after which we continue with the fourth factor, the presence of a catalyst.

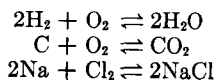
*Influence of the Nature of the Reactants.* The influence of the nature or activity of substances on the speed of reaction is apparent. Silver and iron standing in moist air behave quite differently, although temperature, catalyst, and concentration are uniform for both. The iron continues to unite with oxygen till it is completely converted to rust, whereas the silver does not change appreciably. The nature of these two substances plays an important part in determining the speed of their reactions with oxygen.

In the two opposing reactions discussed at the beginning of this chapter,



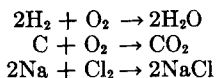
the nature of ammonia molecules is such that they have a moderate tendency to decompose at 200°C and 30 atm. On the other hand, hydrogen and nitrogen molecules have a greater tendency to unite under these conditions, forming ammonia. This is the main reason why the equilibrium mixture has a larger proportion of ammonia (67.6 per cent  $\text{NH}_3$  by volume). That is, the rate of decomposition can equal the rate of formation only when the concentration of the ammonia molecules is sufficiently greater than that of the hydrogen and nitrogen molecules to compensate for the natural tendency of ammonia molecules to decompose slowly.

In many reversible reactions, the tendency for one of the opposing reactions to occur is much greater than it is for the other. In these cases we frequently ignore the slow one, because it has an insignificant effect on the amount of product obtainable from the reaction. Thus, in such chemical changes as



## REACTION RATES; CHEMICAL EQUILIBRIA

the reverse reaction occurs at an extremely slow rate unless the temperature is abnormally high. For all practical purposes we may consider that the forward reaction *goes to completion*, and we indicate this by using a single arrow:



**Influence of Temperature.** The speed of all chemical reactions is increased by an increase in temperature. As a rough guide, it can be said that the speed of a chemical reaction approximately doubles for a rise of 10°C. Actually, the speed of different reactions is affected to a different extent by temperature changes. This means that, in a reversible reaction, the speed of one of the opposing reactions is increased more than that of the other by an increase in temperature. A change in temperature, therefore, changes the relative proportions in an equilibrium mixture.

Let us again consider the reversible decomposition of ammonia. Suppose that the ammonia is placed in a closed container maintained at a certain pressure, is heated, and is held at a certain temperature till equilibrium is established. The amounts of ammonia, hydrogen, and nitrogen present at equilibrium (determined by chemical analysis) are shown in Table 12-1 for different temperatures and pressures. Notice that the amount of ammonia in the equilibrium mixtures is least at the highest temperature. This means that raising the temperature speeds up the decomposition of ammonia more than it speeds up its synthesis. The tendency for ammonia molecules to decompose is so much greater at very high temperatures than that for nitrogen and hydrogen molecules to unite that very little ammonia can be present in the equilibrium mixture.

TABLE 12-1 *Percentage yield by volume of ammonia*

temperature °C	pressure, atm						
	10	30	50	100	300	600	1,000
200	50.7%	67.6%	74.4%	81.5%	90.0%	95.4%	98.3%
300	14.7	30.3	39.4	52.0	71.0	84.2	92.6
400	3.9	10.2	15.3	25.1	47.0	65.2	79.8
500	1.2	3.5	5.6	10.6	26.4	42.2	57.5
600	0.5	1.9	2.3	4.5	13.8	23.1	31.4
700	0.2	0.7	1.1	2.2	7.3	12.6	12.9

SOURCE: A. T. Larson, *J. Am. Chem. Soc.*, **46**:371 (1924).

**Le Chatelier's Principle.** How can we predict which reaction of an opposing pair will undergo the greater change in rate as the result of a change in temperature? A prediction can be made if we know

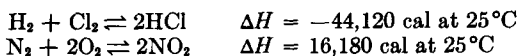
which reaction is endothermic and which is exothermic. In the equilibrium



the union of hydrogen and nitrogen to form ammonia is exothermic (heat is liberated); conversely, the decomposition of ammonia into hydrogen and nitrogen is endothermic. If the temperature of the equilibrium mixture is raised, the endothermic reaction is favored, because it requires heat from the surroundings in order to take place. The exothermic reaction is favored by a decrease in temperature, because this reaction liberates heat to the surroundings and does so more readily if the surroundings are at a low temperature.

The predictions above are applications of Le Chatelier's principle (see Chap. 10). The stress being brought to bear in the case under discussion is the addition or removal of heat energy (temperature change).

Consider these two equilibrium systems:



The union of hydrogen and chlorine to form hydrogen chloride is an exothermic reaction. The higher the temperature, the smaller the percentage of hydrogen chloride in the equilibrium mixture. For, according to Le Chatelier, the reaction that absorbs heat (the decomposition of hydrogen chloride in this case) is favored by the higher temperature.

The union of nitrogen and oxygen to form nitrogen dioxide is an endothermic reaction. On the basis of Le Chatelier's principle, we would predict that higher temperatures favor the formation of nitrogen dioxide. It must be noted, however, that with large changes in temperature the value of  $\Delta H$  will change; also, the influence on the equilibrium of the difference in the entropy of the reactants and products increases as the temperature increases, as we shall see in Chap. 16. Actually, all compounds tend to decompose if the temperature is high enough. At very high temperatures, therefore, the decomposition of nitrogen dioxide is favored.

Le Chatelier's principle can also be used in predicting the influence of pressure on an equilibrium system. This is discussed later in this chapter.

**Influence of Concentration.** The influence of *concentration* can be illustrated by the burning of a piece of wood in pure oxygen and in air. We observe that the wood burns more rapidly in pure oxygen. In pure oxygen, every molecule initially in contact with the wood is an oxygen molecule; but in air, only one molecule out of every five is an oxygen molecule. Because the nitrogen serves as a diluting material, the rate of combustion in air is considerably less than in pure oxygen.

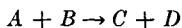
## REACTION RATES; CHEMICAL EQUILIBRIA

The concentration of the wood is equally important in determining the rate of combustion. In a piece of wood, only the molecules in the exposed surface layer are in contact with oxygen molecules and in a position to react at a given time. Because surface area is a measure of available concentration, the rate of burning can be increased by splitting the wood into small pieces.

In order that two or more molecules react, they must come very close together or collide. Consequently, the rate of a reaction would be expected to increase as the molecules are crowded more closely together. There are many ways of expressing the concentration of molecules. The chemist usually prefers to use moles per liter when discussing reaction rates. Since 1 mole contains  $6.02 \times 10^{23}$  molecules, this way of expressing concentration indicates the number of molecules actually present in a unit volume.

A definite relationship exists between the rate of a chemical reaction and the concentration of the reactants. This relationship is known as the law of mass action: *The rate or speed of a chemical reaction is proportional to the concentration of each of the reactants.* We shall discuss this in terms of two hypothetical reactions.

1. In the reaction between  $A$  and  $B$  to produce  $C$  and  $D$ ,



the speed is proportional to the number of moles per liter of  $A$ . The speed is also proportional to the number of moles per liter of  $B$ . If the number of molecules of  $A$  in 1 liter is doubled and the number of  $B$  molecules is trebled, the rate will be six times faster. These statements are expressed mathematically thus:

$$R_f \propto [A] \times [B]$$

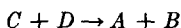
$R_f$  is the rate of the forward reaction,  $\propto$  means "is proportional to," and the brackets signify "moles per liter" of  $A$  and  $B$ .

Because the rate is also dependent on other factors—namely, the nature of  $A$  and  $B$  and the temperature—it is necessary to add a term to the proportionality if the proportionality sign is to be replaced by an equality sign:

$$R_f = k \times [A] \times [B]$$

This expression states that the rate of the reaction is equal to some quantity  $k$  (determined by the nature of  $A$  and  $B$  and by the temperature) multiplied by the number of moles per liter of  $A$  and the number of moles per liter of  $B$ . Once the reactants have been chosen, their nature is fixed. Consequently, the magnitude of  $k$  for a given reaction at a given temperature does not change. This quantity  $k$  is referred to as the **rate constant** for the reaction.

We next consider the reverse reaction:

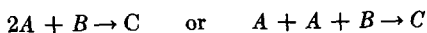


The rate of the reverse reaction is given by the expression

$$R_r = k' \times [C] \times [D]$$

The numerical value of  $k'$  is not the same as that of  $k$ , because the nature of  $C$  and  $D$  differ from that of  $A$  and  $B$ .

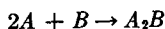
2. Consider the reaction



In this case, the speed of the reaction is proportional to the square of the concentration of  $A$ , for it is necessary that 2 molecules of  $A$  collide for the reaction to occur. The reaction rate is

$$\begin{aligned} R &= k \times [A] \times [A] \times [B] \\ R &= k \times [A]^2 \times [B] \end{aligned}$$

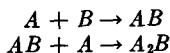
*Rate-determining Step.* From what has been said thus far, it appears that the rate of a chemical reaction is proportional to each reactant's concentration raised to the power corresponding to the number of molecules shown in the balanced equation. This is not often true, because an equation does not necessarily represent the true course of the reaction; that is, the reaction may take place in steps, so that actually two or three reactions have occurred before the final products are reached. To illustrate these points let us consider the reaction



If, in order for the reaction to occur, 2 molecules of  $A$  and 1 of  $B$  must collide simultaneously, the reaction is a one-step process, and the rate is given by

$$R = k \times [A]^2 \times [B]$$

However, experimental work proves that very few reactions take place through the simultaneous collision of 3 molecules. For example, the reaction under discussion might occur in the following steps:



Of these two, the slower reaction is referred to as the *rate-determining reaction*, because the speed of the overall reaction is determined by the speed of the slower step. Consequently, if the first reaction above is the rate-determining reaction for the overall reaction  $2A + B \rightarrow A_2B$ , the speed is given by

$$R = k \times [A] \times [B]$$

rather than by

$$R = k \times [A]^2 \times [B]$$

Therefore, we cannot predict solely from a balanced chemical equation how the reaction rate will be influenced by the concentrations of the reactants. The relationship must be determined experi-



## REACTION RATES; CHEMICAL EQUILIBRIA

mentally. In many reactions whose rates have been determined, the rates are proportional to the first power of the concentration of each reactant.

### ORDER OF A CHEMICAL REACTION

If the rate of a chemical reaction is proportional to the concentration of just one reactant,

$$R = k \times [A]$$

the reaction is said to be a **first-order reaction**. If the rate of a reaction is proportional to the product of the concentration of two reactants

$$R = k \times [A] \times [B]$$

or if it is proportional to the concentration squared of one reactant,

$$R = k \times [A]^2$$

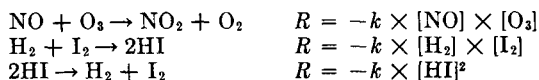
the reaction is said to be a **second-order reaction**. The order of a reaction is the sum of the powers of the concentrations as expressed in the rate equation. A reaction can be of third order or possibly higher, but such cases are rare. In complicated reactions, the rate may be of fractional order, for example, of 1.5 order.

The simplest type of first-order reaction is one in which there is just one reactant that is decomposing. The following reactions are examples of this type:



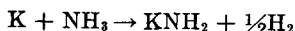
The minus sign indicates that the amount of the reactant is decreasing with time, and the reaction is slowing down. One of the most interesting first-order processes that we shall study is that of radioactive decay, which is taken up in Chap. 14.

The following equations represent examples of second-order reactions:



The order of a reaction is assigned only on the basis of an experimental determination that the rate of the reaction is actually proportional to the concentrations of certain reactants. Theoretical predictions about orders of unfamiliar reactions are seldom successful. For instance, knowing that the reaction between  $\text{H}_2$  and  $\text{I}_2$  is second order, one would predict that the reaction between  $\text{H}_2$  and  $\text{Br}_2$  would be second order also. It is not but instead has a more complex rate equation.

present in such large amounts that its concentration does not change appreciably. The reaction between elemental potassium and liquid ammonia is an example:



A very small amount of potassium is dissolved in the liquid ammonia (enough to make about  $1 \times 10^{-3}M$  solution). Therefore, the amount of ammonia present,  $\text{NH}_3$ , is practically the same from start to finish during the reaction. The rate equation possibly could be written

$$R = -k' \times [\text{K}] \times [\text{NH}_3]$$

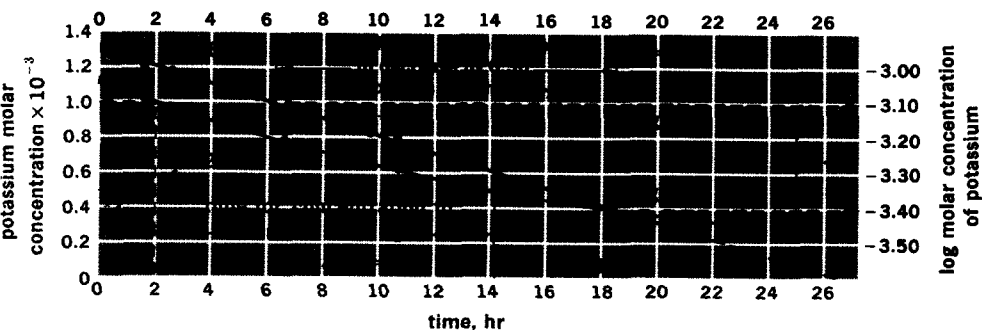
but because  $[\text{NH}_3]$  is a constant, the product of  $k'[\text{NH}_3]$  is also a constant,  $k$ , so that the rate equation is written

$$R = -k \times [\text{K}]$$

The rate of this reaction is determined experimentally by determining the change in color of the solution with time. The reactant solution, an intense blue at the beginning, slowly fades in color and becomes practically colorless as the reaction approaches equilibrium. The amount of unreacted potassium remaining in solution at any time is determined from the depth of color left. The measurements are made with sensitive photoelectric cells.

A reaction, like the one just discussed, that appears to be first order although it probably involves two or more reacting species, is called **pseudo first order**.

Irrespective of whether a reaction is truly first order or is pseudo first order, the rate equation has the same form. The characteristic



Half-life of a first order reaction. The black line, plotted from experimental data, shows how the concentration (left ordinate) changes with time. To determine the half-life, one chooses a point easily read on the black line, say  $1 \times 10^{-3}$  mole at 2 hr, and then follows the black line to the point which represents half of this concentration,  $0.5 \times 10^{-3}$ . This concentration existed at 14.2 hr, so  $t_{1/2} = 12.2$  hr. The blue line shows the same information, except that the logarithm of the concentration (right ordinate) is plotted versus the time. Since the logarithm plot gives a straight line, the graph can usually be constructed more precisely from less experimental information than when the concentration is plotted directly.

FIG. 12-2

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rate of decrease in concentration for first-order reactions is shown in two ways in Fig. 12-2. The data plotted are listed in Table 12-2. Figure 12-2 shows that the rate decreases with the passage of time. This is because the concentration of potassium is decreasing, and the rate of the reaction is directly proportional to the potassium concentration. As shown by the plot, there is a certain time interval for a first-order reaction, called the *half-life*, for any given concentration to fall to one-half of that concentration. For a rapid reaction, the half-life can be a small fraction of a second; for a slow reaction, it can be years.

Because the first-order rate is proportional to  $[K]$ , as shown by Fig. 12-2, as  $[K]$  becomes smaller, so does the rate of reaction. The rate appears to approach zero but never to attain it, as shown by the black curve in Fig. 12-2. Practically, the amount of change in the reactant remaining after several half-lives becomes so small that it cannot be measured; the reaction is then over, or the system is at equilibrium.

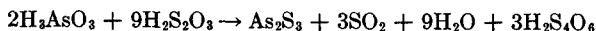
**TABLE 12-2** *Change in molar concentration of potassium with time during reaction  $K + NH_3 \rightarrow K^+ + NH_2^- + \frac{1}{2}H_2$*

hrs	time min	sec	intensity of color	molar concentration	log molar concentration
		18	1.702	$1.13 \times 10^{-3}$	-2.947
	31	41	1.641	1.09	-2.963
1	0		1.588	1.05	-2.978
1	33		1.552	1.03	-2.987
2	33		1.476	$9.80 \times 10^{-4}$	-3.009
3	33		1.427	9.46	-3.024
4	34		1.322	8.77	-3.057
5	34		1.252	8.32	-3.080
6	36		1.196	7.94	-3.100
7	35		1.108	7.35	-3.134
9	38		0.996	6.62	-3.179
10	39		0.948	6.29	-3.201
12	31		0.841	5.59	-3.253
21	26		0.506	3.36	-3.474

In Fig. 12-2, the logarithm of the potassium concentration is plotted against the time. For a first-order reaction this plot is a straight line, which shows that a direct proportion exists. The equation that shows that for a first-order rate the change in the log of the concentration is directly proportional to the change in the time elapsed is derived by applying calculus to the study of reaction rates. Other graphical methods and other equations have been developed for studying second-order and more complex reactions. The investigation of rates of reactions has led to many discoveries about the ways in which molecules, ions, and atoms interact with one another.

**CLOCK REACTION.** A fascinating type of reaction is one in which for a time there is no visible evidence that a reaction is taking place, and then suddenly a major change occurs such as a color appearing or a precipitate forming. Some of these reactions are complex, although they may follow a simple rate equation.

When arsenious acid,  $\text{H}_3\text{AsO}_3$ , reacts with a solution of thiosulfuric acid,  $\text{H}_2\text{S}_2\text{O}_3$ , nothing is observed to happen for several seconds or minutes; then suddenly a voluminous precipitate of yellow arsenious sulfide,  $\text{As}_2\text{S}_3$ , appears. This reaction is undoubtedly complicated, so much so that chemists disagree about how the overall equation should be written. One suggestion is



By measuring the time that it takes for the  $\text{As}_2\text{S}_3$  precipitate to form in solutions of different concentrations of  $\text{H}_2\text{S}_2\text{O}_3$ , it can be shown by plotting time against concentration that the reaction rate is directly proportional to the concentration of the thiosulfate ion:

$$R = k \times [\text{S}_2\text{O}_3^{2-}]$$

The reaction is pseudo first order.

## EQUILIBRIUM CONSTANT

At equilibrium, the speed of the forward reaction is equal to the speed of the reverse reaction:

$$R_f = R_r$$

For the reactions  $A + B \rightleftharpoons C + D$ ,

$$R_f = k \times [A] \times [B]$$

$$R_r = k' \times [C] \times [D]$$

then at equilibrium

$$k \times [A] \times [B] = k' \times [C] \times [D]$$

Rearranging, we obtain

$$\frac{k}{k'} = \frac{[C] \times [D]}{[A] \times [B]}$$

For a given reaction at a specific temperature, the quantities  $k$  and  $k'$  do not change. Because a constant divided by a constant must also be a constant,<sup>1</sup> we may replace  $k/k'$  by the term  $K$ :

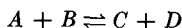
$$K = \frac{[C] \times [D]}{[A] \times [B]}$$

The quantity  $K$  is called the **equilibrium constant**. The numerical value of  $K$  does not change so long as we are dealing with the same equilibrium system at a given temperature.

<sup>1</sup> Consider  $k/k'$ . If  $k$  is 6 and  $k'$  is 4, then  $k/k'$  must be 1.5. So long as  $k$  and  $k'$  do not change,  $k/k'$  cannot change:  $k/k' = K$ .

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However, concentrations can be varied as desired. For example, if more  $A$  is added to the equilibrium mixture



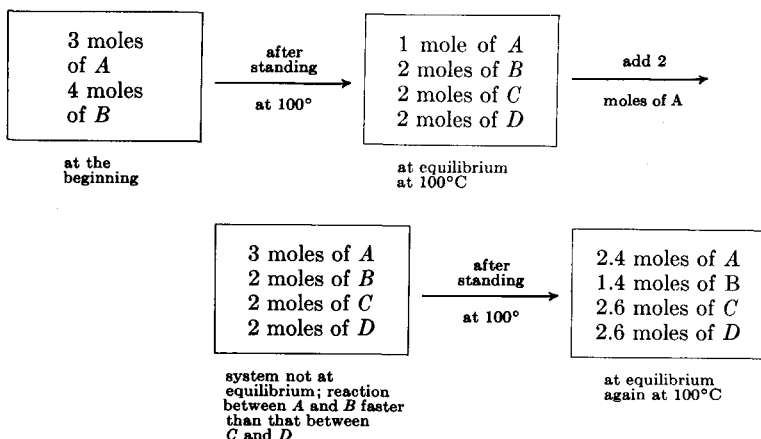
the system is not at equilibrium momentarily, because the speed of the forward reaction is increased by the added  $A$ . The system will return to equilibrium, because  $A$  and  $B$  are being used up more rapidly than they are being formed by the reverse reaction, and the speed of the reverse reaction gradually increases, because  $C$  and  $D$  are being formed more rapidly than they are reacting. Eventually the two reaction rates become equal again.

When the new equilibrium state is attained, the concentrations of  $A$  and  $B$  and of  $C$  and  $D$  will all have changed. But if these new concentrations are placed in the equilibrium constant equation and the equation is solved for  $K$ , its value will be found to be unchanged:

$$K = \frac{[C] \times [D]}{[A] \times [B]}$$

The validity of these conclusions has been tested many times by experiments. The following hypothetical experiment illustrates the method.

Three moles of  $A$  and 4 moles of  $B$  are placed in a liter container. The mixture is held at a constant temperature of  $100^{\circ}\text{C}$  till equilibrium is reached. The quantities of  $A$ ,  $B$ ,  $C$ , and  $D$  in the equilibrium mixture are determined by analysis to be 1 mole of  $A$ , 2 moles of  $B$ , 2 moles of  $C$ , and 2 moles of  $D$ . To this equilibrium mixture, 2 additional moles of  $A$  is added; when the system again comes to equilibrium at  $100^{\circ}\text{C}$ , it is found by analysis to contain 2.4, 1.4, 2.6, and 2.6 moles of  $A$ ,  $B$ ,  $C$ , and  $D$ , respectively. The hypothetical experiments can be represented diagrammatically in this way:



On calculating the value for  $K$  for the first equilibrium mixture, we find

$$K = \frac{[C] \times [D]}{[A] \times [B]} \\ = \frac{2 \times 2}{1 \times 2} \\ = 2$$

On calculating the value for  $K$  for the second equilibrium, we find

$$K = \frac{2.6 \times 2.6}{2.4 \times 1.4} \\ = 2$$

The value of  $K$ , the equilibrium constant, did not change, although all the individual concentrations did.

Here are examples of  $K$  for various actual equilibria.

For  $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$

$$K = \frac{[\text{H}_2]^2 \times [\text{O}_2]}{[\text{H}_2\text{O}]^2}$$

For  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2] \times [\text{H}_2]^3}$$

For  $\text{CH}_3\text{OH} + \text{HCl} \rightleftharpoons \text{CH}_3\text{Cl} + \text{HOH}$

$$K = \frac{[\text{CH}_3\text{Cl}] \times [\text{HOH}]}{[\text{CH}_3\text{OH}] \times [\text{HCl}]}$$

In writing the expression for an equilibrium constant, the concentrations of the substances on the right of the double arrows are always in the numerator.

Note that the concentration of each reactant is raised to the power corresponding to the number of molecules in the balanced equation. This appears contradictory to the statement made earlier that the reaction rate is not necessarily proportional to the concentration raised to the power indicated by the balanced equation. However, the power relationship is valid for the equilibrium constant expression, because factors in the rate expressions for the opposing reactions always cancel in such a way as to give the indicated expression for the equilibrium constant.

The equilibrium constant  $K$  is commonly evaluated in terms of concentrations expressed in moles per liter, as indicated by our use of square brackets, [ ]. However, for equilibrium systems involving gases it is also common to calculate an equilibrium constant by expressing the amounts of the substances in terms of partial pressures. The constant evaluated in this way, called  $K_p$ , is numerically related to  $K$ , because the partial pressure of a gas is directly proportional to its concentration in moles per liter.<sup>1</sup> In the reaction  $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$ ,

<sup>1</sup> If the number of moles of products and reactants are equal,  $K_p = K$ .

with the following relationship of partial pressures,

$$\text{total pressure, atm} = p_{\text{H}_2\text{O}} + p_{\text{H}_2} + p_{\text{O}_2}$$

the value of  $K_p$  is calculated as

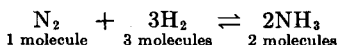
$$K_p = \frac{p_{\text{H}_2}^2 \times p_{\text{O}_2}}{p_{\text{H}_2\text{O}}}$$

Values of  $K$  have been experimentally determined for a great number of equilibrium systems and are recorded in the chemical literature. For a system in which the forward reaction goes nearly to completion,  $K$  is very large. Conversely, if the forward reaction takes place to a very slight extent as compared with the reverse reaction,  $K$  is very small.

## INFLUENCE OF PRESSURE

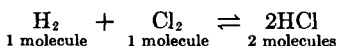
Pressure influences the speed of a reaction only in so far as pressure changes bring about changes in concentration. Increasing the pressure on a liquid or solid does not appreciably crowd the molecules closer together and therefore has little effect on the speeds of chemical reactions involving only liquids or solids. On the other hand, when the pressure of a gas is increased, the concentration (moles per liter) is proportionately increased. Consequently, pressure changes have a marked influence on the speeds of reactions involving gases and hence may influence an equilibrium system made up of gases. We should emphasize at the outset of this discussion of reactions involving gases that a change in pressure can affect the relative amounts of reactants and products at equilibrium, but a change in pressure does not change the value of the equilibrium constant.

According to Le Chatelier's principle, if the pressure is changed on a system at equilibrium, the reaction that tends to diminish the change in pressure is favored. The effect of added pressure is to increase the crowded condition of the molecules. The reaction that produces the fewer number of molecules (and therefore tends to lower the pressure) is the reaction favored by high pressures. In the equilibrium system

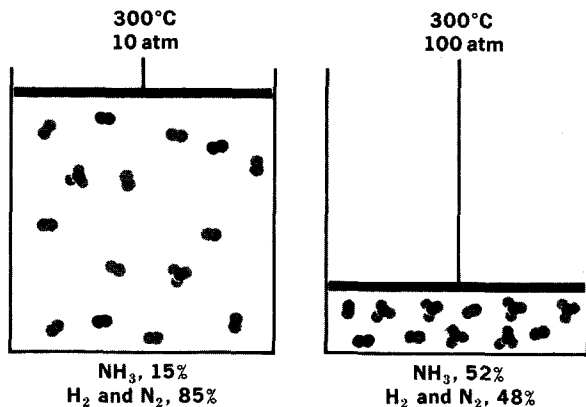


the forward reaction brings about a decrease in the total number of molecules in the container. The reverse reaction (decomposition of ammonia molecules) increases the total number of molecules. If equilibrium is established at a relatively low pressure, the equilibrium mixture contains a smaller proportion of ammonia and a larger proportion of nitrogen and hydrogen as compared with the amounts present at a higher pressure. This is illustrated diagrammatically in Fig. 12-3.

In the equilibrium



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An illustration of Le Chatelier's principle. An increase in pressure favors the reaction which produces the fewer molecules.

a change in pressure has no influence on the relative amounts in the equilibrium mixture. This is because the reactions produce no change in the total number of molecules present.

That a variation in pressure can change the relative amounts of reactants and products without changing the value of the equilibrium constant is difficult to visualize. An example or two will make this clearer.

**Actual Example.** In Table 12-1 the experimental data for the ammonia synthesis enable us to calculate  $K_p$  under different conditions. To investigate the effect of pressure, let us calculate  $K_p$  at 10 and 100 atm, keeping the temperature constant at 400°.

$K_p$  at 10 atm:

$$\begin{aligned}\text{total pressure} &= 10 \text{ atm} = p_{\text{NH}_3} + p_{\text{H}_2} \text{ and } \text{N}_2 \\ p_{\text{NH}_3} &= 3.9\% \text{ of total pressure} \\ &= 0.039 \times 10 \text{ atm} \\ &= 0.39 \text{ atm} \\ p_{\text{H}_2} \text{ and } \text{N}_2 &= 10 \text{ atm} - 0.39 \text{ atm} = 9.61 \text{ atm}\end{aligned}$$

Since the molecules of H<sub>2</sub> and N<sub>2</sub> are in a 3:1 ratio,

$$\begin{aligned}p_{\text{H}_2} &= \frac{3}{4} \times 9.61 \text{ atm} = 7.21 \text{ atm} \\ \text{and} \quad p_{\text{N}_2} &= \frac{1}{4} \times 9.61 \text{ atm} = 2.40 \text{ atm}\end{aligned}$$

$$\begin{aligned}K_p &= \frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} \times p_{\text{H}_2}^3} \\ &= \frac{0.39^2}{2.40 \times 7.21^3} = 1.7 \times 10^{-4}\end{aligned}$$

$K_p$  at 100 atm:

$$\begin{aligned}p_{\text{NH}_3} &= 25.1\% \text{ of total pressure} \\ &= 0.251 \times 100 \text{ atm} = 25.1 \text{ atm} \\ p_{\text{N}_2} &= \frac{1}{4} (100 - 25.1) = 18.7 \text{ atm} \\ p_{\text{H}_2} &= \frac{3}{4} (100 - 25.1) = 56.2 \text{ atm} \\ K_p &= \frac{25.1^2}{18.7 \times 56.2^3} = 1.9 \times 10^{-4}\end{aligned}$$

FIG. 12-3

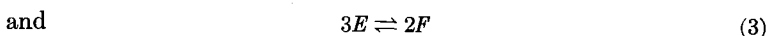
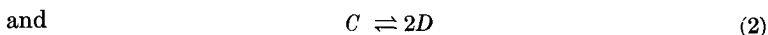


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In the second case, with the pressure increased by 10 times, the percentage of ammonia in the equilibrium mixture was increased by 6.4 times, but the value of  $K_p$  changed very little.

The small change in  $K_p$  illustrated in the two foregoing calculations is typical of many "constant" relationships in physical and chemical changes. The value of the equilibrium constant is not absolutely unchanging, but it is nearly so. Calculations at higher pressures do not give such good agreement. The value of  $K_p$  becomes less "constant" because the gases behave less like ideal gases as they are crowded together at high pressure. To determine the true equilibrium constant at any temperature, the value of  $K_p$  is evaluated at several low total pressures; then a plot is made and extrapolated to zero pressure to evaluate the ideal  $K_p$ .

*Hypothetical Examples.* To illustrate the effect of changes in concentration (or pressure) on the *relative amounts* of reactants and products in equilibrium systems, let us consider some possible chemical equilibria that involve only two gaseous substances,  $A$  and  $B$ , or  $C$  and  $D$ , etc. Among the possible systems we could choose are



For each of these equilibria we can write the expression for the equilibrium constant:<sup>1</sup>

$$K' = \frac{[B]}{[A]} \quad (4)$$

$$K'' = \frac{[D]^2}{[C]} \quad (5)$$

$$K''' = \frac{[F]^2}{[E]^3} \quad (6)$$

To calculate the effect of changing concentrations, let us imagine that each gaseous mixture is quickly compressed to one-half of its volume, thus doubling the concentration (or pressure) of each constituent. For reaction (1), the right-hand expression of Eq. (4) becomes

$$\frac{2[B]}{2[A]}, \text{ which is } \frac{[B]}{[A]}, \text{ which does equal } K'$$

This shows that changing  $[A]$  and  $[B]$  by equal amounts in the case of reaction (1) does not change the relative amounts of  $A$  and  $B$  at equilibrium; the new, more concentrated system still satisfies the equilibrium condition.

<sup>1</sup> Similar expressions could be written for  $K_p$  by merely substituting  $p_A$  for  $[A]$ ,  $p_B$  for  $[B]$ , etc.

For reaction (2), on doubling the concentrations, the right-hand expression of Eq. (5) becomes

$$\frac{[2D]^2}{[2C]}, \text{ which is } \frac{4[D]^2}{2[C]} \text{ or } 2 \frac{[D]^2}{[C]}, \text{ which does not equal } K''$$

This shows that changing  $[C]$  and  $[D]$  by equal amounts in the case of reaction (2) produces a system that initially is not in equilibrium. Chemical reactions must now take place that tend to establish a new equilibrium; in this case what is needed is relatively more  $C$  and less  $D$ . We can see from the form of Eq. (5) that, to maintain  $[D]^2/[C]$  constant, for any given amount of increase in  $C$ , the increase in  $D$  is the square root of that amount. For instance, if  $[C]$  is increased by 5 times,  $[D]$  is increased by  $\sqrt{5}$  (or  $5^{1/2}$ ) times, and the right-hand expression of Eq. (5) reads

$$\frac{[\sqrt{5}D]^2}{[5C]} = \frac{5[D]^2}{5[C]} = \frac{[D]^2}{[C]}, \text{ which does equal } K''$$

For reaction (3), on doubling both concentrations, the right-hand expression of Eq. (6) becomes

$$\frac{[2F]^2}{[2E]^3}, \text{ which is } \frac{4[F]^2}{8[E]^3} \text{ or } \frac{1}{2} \frac{[F]^2}{[E]^3}, \text{ which does not equal } K'''$$

From the form of Eq. (6), we see that for a given amount of change in  $F$ , the change in  $E$  is the three-halves root of that amount in order to maintain  $[F]^2/[E]^3$  constant. For instance, if  $F$  is increased by 2 times,  $E$  must be increased by  $2^{2/3}$  times (that is, 1.587 times) to achieve a system in equilibrium. The right-hand expression reads

$$\frac{[2F]^2}{[2^{2/3}E]^3} = \frac{4[F]^2}{4[E]^3} = \frac{[F]^2}{[E]^3}, \text{ which does equal } K'''$$

We may summarize as follows. In a gaseous system, if the total number of moles of reactants equals the total number of moles of products, the relative amounts at equilibrium are not changed by changes in pressure; if the total number of moles of reactants does not equal the total number of moles of products, the relative quantities must change when changes in pressure occur. In all such changes, the equilibrium constant does not change.

## INFLUENCE OF A CATALYST

A catalyst is a substance that alters the speed of a chemical reaction without itself undergoing a permanent chemical change. The process is called catalysis. Catalysts are usually employed to increase the speed of the chemical reaction desired. Not infrequently, however, a substance is used to retard the rate of a chemical reaction. The uses of certain substances in antifreezes to retard rusting, in rubber to retard aging, and in hydrogen peroxide to retard decomposition are examples

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of the uses of catalysts to slow down undesirable reactions. The substances employed for this purpose are referred to as *inhibitors*, although the term *negative catalyst* has also been used.

In an equilibrium system, a catalyst alters the speed of both forward and reverse reactions to the same extent. A catalyst does not change the relative amounts present at equilibrium; the value of the equilibrium constant is not changed. The catalyst does change the time required for establishing the equilibrium. Reactions that require days or weeks to come to equilibrium may reach it in a matter of minutes in the presence of a catalyst.

Furthermore, reactions that proceed at a suitable rate only at very high temperatures may proceed rapidly at much lower temperatures when a catalyst is used. This is especially important if high temperatures decrease the yield of the desired products. The synthesis of ammonia is a case in point. In the absence of a catalyst the reaction between hydrogen and nitrogen is so slow, even at temperatures above  $100^{\circ}$ , that the reaction might take years to reach equilibrium. The data shown in Table 12-1 were determined in the presence of a catalyst.

### HOW CATALYSTS CHANGE THE SPEEDS OF CHEMICAL REACTIONS

A catalyst is thought to influence the speed of a chemical reaction in one of two ways: (1) by the formation of intermediate compounds or (2) by adsorption.

*By the Formation of Intermediate Compounds.* In a given number of molecules at a specified temperature, the majority have normal velocities or kinetic energies. Because of collisions, a few of the molecules have large amounts of energy. These molecules are *energy-rich* as compared with their neighbors. There is also a small percentage of

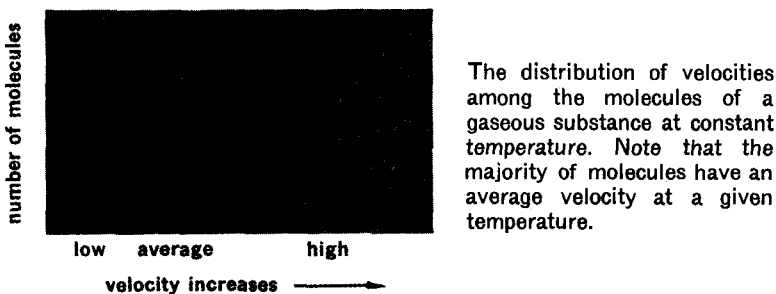


FIG. 12-4

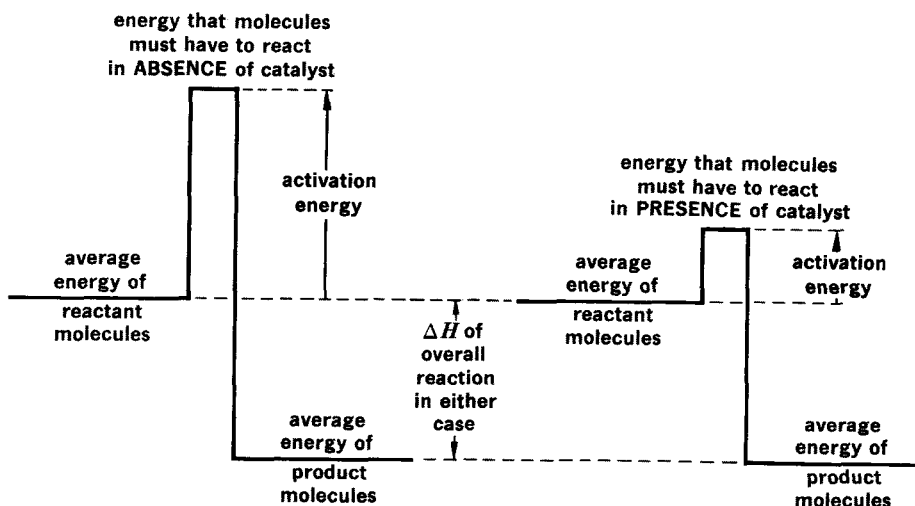
molecules that is *energy-poor*. The probable distribution of velocities among the molecules at a specified temperature is described by a *distribution curve* like that in Fig. 12-4. According to this curve, most

of the molecules in a system have velocities close to some average value; only a few have extremely low velocities (energy-poor), and only a few have extremely high velocities (energy-rich).

If we are dealing with a reaction that takes place only between molecules with high energy, the reaction may be quite slow at normal temperatures, because only a small percentage of the molecules has sufficiently high energy to react. The molecules having normal energies simply collide and rebound without reacting. The extra energy that two molecules must have to take part in a chemical reaction is called the **activation energy** of the reaction.

The situation is somewhat like that involved in automobiles going over a mountain. If the road leads directly up and across, only the cars with extremely powerful engines can make it. If the road leads through a gap in the mountain, all the cars can go over. Similarly, when we are dealing with a reaction that requires a high activation energy, if we can provide a path for the reaction so that molecules with lower energy can react, more of the molecules can participate. The reaction then takes place faster.

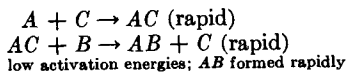
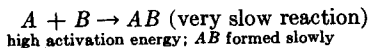
How can the path of the reaction be changed? It may be that a substance, that is, a catalyst, can be found that reacts alike with energy-poor and energy-rich molecules to form an **intermediate compound** that in turn reacts to form the desired substance. If the energy requirements for both these reactions are low, more of the molecules can participate at any given time (Fig. 12-5). These reactions may be generalized as follows, *C* representing the catalyst:



A reaction requiring high-energy molecules proceeds slowly. A catalyst lowers the activation energy so that more molecules can participate in the reaction at a given temperature.

FIG. 12-5

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It will be noted that  $C$  does not undergo a permanent change; it can be used over and over. The intermediate compound  $AC$  usually has only a temporary existence, being used up as rapidly as it is formed. Many chemical reactions are known to follow such a path when a catalyst is used. Sometimes the intermediate compound  $AC$  can be obtained in small quantities.

**By Adsorption.** Many solid substances that act as catalysts can hold appreciable quantities of gases and liquids on their surfaces; as pointed out in Chap. 11, this is known as adsorption. For a solid to be an effective adsorbing agent, it must be in a finely divided or expanded state, so that a large amount of surface is present. Finely divided nickel and platinum are well known for their ability to adsorb large amounts of various gases. The adsorbed molecules are frequently more reactive than the unadsorbed molecules. This increased reactivity can be attributed in some cases to the increased concentration of the adsorbed molecules; they are crowded close together on the surface of the solid, whereas in the gaseous state they are far apart. In other cases, the attractive forces between the molecules of the solid and those of the adsorbed liquid or gas make the adsorbed molecules more active chemically. This causes the reaction between molecules  $A$  and  $B$  to take place on the surface of the solid at a faster rate than if the catalyst were not present. (See Figs. 12-6 and 12-7). The catalyst must not adsorb the product of the reaction. As the reaction proceeds, the product leaves the surface and more reactants are adsorbed. Thus the surface is used over and over.

The hydrogenation of liquid fats to form solid fats is carried out on the surface of finely divided nickel. The oxidation of sulfur dioxide to sulfur trioxide on a platinum surface (in the production of sulfuric acid) is another case in which a catalyst influences the speed of a reaction by adsorption.

It might be pointed out that catalytic activity is specific in nature. A catalyst that accelerates a particular reaction may have no influence on another reaction.

## INFLUENCE OF TEMPERATURE

We have discussed the influence of several factors on equilibrium systems. Catalysts can change the rate at which equilibrium is attained, but they do not change the value of the equilibrium constant. Changes in pressure or in concentration can change the relative amounts of reactants and products, but they do not change the value of the equilibrium constant.

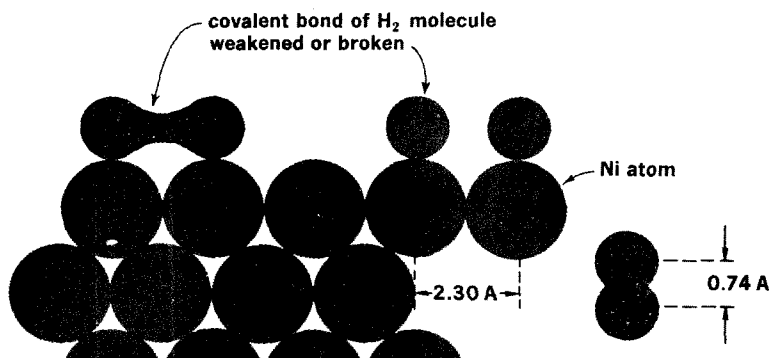


FIG. 12-6

Catalytic action by adsorption. Note that the interatomic dimensions are such that the bond in an H<sub>2</sub> molecule is probably stretched or broken when hydrogen is adsorbed on nickel. According to one theory, this accounts for the greater activity of hydrogen in catalyzed hydrogenation reactions.

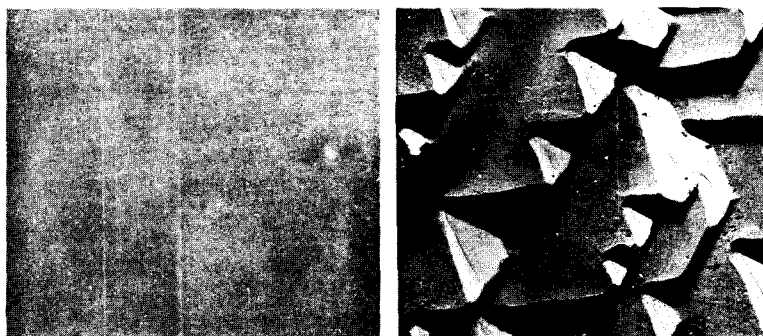
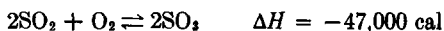


FIG. 12-7

The caption of Fig. 12-6 suggested that the attractive forces between adsorbed molecules and a catalyst may cause a weakening of bonds in the substance adsorbed. These forces may cause a considerable change in the catalyst also, even though the net weight of the catalyst remains constant. The left photograph shows the polished surface of a copper catalyst before use (70,000 magnification). At the right is shown the surface (3000 magnification) of the copper as it appeared after use. This sample of copper was used continuously for seven days at 400°C to catalyze the reaction of hydrogen and oxygen to form water. (Courtesy of Professor Allan T. Gwathmey, University of Virginia.)

The temperature, however, is quite a different kind of change. A change in temperature affects the relative stabilities of reactants and products; therefore, a variation in temperature changes the value of the equilibrium constant itself. Data from an important commercial reaction, the production of sulfur trioxide, illustrate this point as we can see in Table 12-3. For the reaction



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the equilibrium constant is

$$K_p = \frac{p^2_{\text{SO}_3}}{p^2_{\text{SO}_2} \times p_{\text{O}_2}}$$

As the temperature is increased, the shift toward the formation of more  $\text{SO}_2$  and  $\text{O}_2$  at the expense of  $\text{SO}_3$  causes the numerator of this expression to decrease and the denominator to increase;  $K_p$  thus becomes lower. The decrease in  $K_p$  with increase in temperature, clearly shown in Table 12-3, is characteristic of an exothermic reaction, as we expect from Le Chatelier's principle.

**TABLE 12-3** *Effect of temperature on equilibrium constant for*  
 $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3 + \text{heat}$

temperature, °C	$K_p$	temperature, °C	$K_p$
400	397	800	0.915
500	48.1	900	0.384
600	9.53	1000	0.184
700	2.63	1100	0.098

As a second example we can refer again to the data on the ammonia synthesis in Table 12-1. We have previously calculated that  $K_p$  at  $400^\circ$  is about  $1.8 \times 10^{-4}$ . Let us now calculate a value at  $500^\circ$ :

Data: Temperature  $500^\circ$ , pressure 10 atm, yield of  $\text{NH}_3$  is 1.2 per cent of total pressure.

$$\begin{aligned} p_{\text{NH}_3} &= (0.012) (10 \text{ atm}) = 0.12 \text{ atm} \\ p_{\text{N}_2} &= \frac{1}{4} (9.88 \text{ atm}) = 2.47 \text{ atm} \\ p_{\text{H}_2} &= \frac{3}{4} (9.88 \text{ atm}) = 7.41 \text{ atm} \\ K_p &= \frac{0.12^2}{2.47 \times 7.41^3} \\ &= 1.4 \times 10^{-5} \end{aligned}$$

For the ammonia system at  $500^\circ$  and 10 atm pressure, the value of  $K_p$  is  $1.4 \times 10^{-5}$ . As in the case of the formation of sulfur trioxide, the formation of ammonia is exothermic, so the lower value of  $K_p$  at  $500^\circ$  as compared with  $400^\circ$  is expected.

It is worth emphasizing the point that, in the ammonia synthesis, with a change in pressure of 10 times,  $K_p$  remains practically constant (see calculations of  $K_p$  at 10 atm and 100 atm on page 307), whereas a change in absolute temperature by a factor of only 1.15 times, from 673 to 773°K, changes the value of  $K_p$  by a factor of about 12 times, from about  $1.8 \times 10^{-4}$  to about  $1.4 \times 10^{-5}$ .

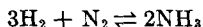
## CHAPTER REVIEW

### Terms

Reversible reactions, equilibrium, rate of reaction, Le Chatelier's principle, rate constant, rate-determining step, order of reaction, clock reaction, equilibrium constant,  $[ ]$ ,  $K$ ,  $K_p$ , catalyst, intermediate compound, activation energy, adsorption.

### Exercises

- Why is a chemical equilibrium referred to as a dynamic equilibrium rather than a static equilibrium?
- Of the factors that influence the speed of a chemical reaction, which can be varied at will? Which are fixed and invariable for a given system?
- What is the molar concentration of a gas that is at a pressure of 10 atm at 0°C?
  - What is the molar concentration of gaseous hydrogen if 10 g are held in a liter flask?
  - What is the molar concentration of gaseous ammonia if 10 g are held in a liter flask?
  - Does 10 g of methanol ( $\text{CH}_3\text{OH}$ ) dissolved in 100 ml aqueous solution have the same molarity as 10 g of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ )?
- At 700°C, hydrogen and oxygen have a great tendency to unite to form water, whereas water has little tendency to decompose into hydrogen and oxygen. Explain how it is possible for hydrogen and oxygen to be combining to form water at the same rate that water is decomposing into hydrogen and oxygen, both reactions taking place in the same container at 700°C.
- If prior to reaction a 3:1 mixture (by volume) of hydrogen and nitrogen occupies a volume of 1 liter at 30 atm and 200°, what will be the volume occupied by the equilibrium mixture



at the same pressure and temperature, if the ammonia exerts 67.6 per cent of the pressure at equilibrium?

- For each of the following reactions write an expression for the rate of the reaction, ignoring the possibility of a rate-determining step. State the order of the reaction as indicated by your hypothetical rate equation. Finally, indicate for each of your written expressions why it might not be valid because of the existence of some rate-determining step or other complication.
  - $\text{N}_2 + 2\text{O}_2 \rightarrow 2\text{NO}_2$  (all are gases)
  - $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$  (all are gases)
  - $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \rightarrow 2\text{C}_6\text{H}_{12}\text{O}_6$  (in dilute aqueous solution)

- Consider the following reaction involving two gases reacting to give a third:



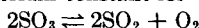


## REACTION RATES; CHEMICAL EQUILIBRIA

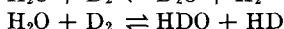
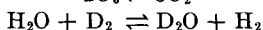
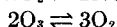
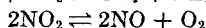
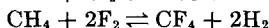
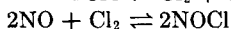
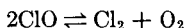
This reaction takes place readily at 500° in the presence of a catalyst. Under the same conditions the following reaction takes place:



- Write the expressions for the rates of reactions (1) and (2),  $R_{(1)}$  and  $R_{(2)}$ , respectively. (Disregard any rate-determining steps.)
- Consider that  $\text{SO}_2$  and  $\text{O}_2$  are brought together at 500° and in the presence of a catalyst. Will the rate expressions written in (a) change as the reactions proceed? Will the numerical values of  $R_{(1)}$  and  $R_{(2)}$  change? Explain. What is the actual value of  $R_{(2)}$  at the instant the  $\text{SO}_2$  and  $\text{O}_2$  are brought together? How might the magnitudes of  $R_{(1)}$  and  $R_{(2)}$  compare 24 hr later? (Temperature is held at 500°C.)
- Show how to combine the expressions you wrote in (a) to arrive at the expression for the equilibrium constant for

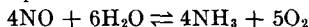


- Write the expression for the equilibrium constant for each of the following equilibria:



- For many reactions the question of the precise position of equilibrium is important in calculating the amounts of products, although in other reactions it is not. Explain, and give examples of both types.
- For a first-order reaction the product of the half-life multiplied by the rate constant equals a constant, 0.693 (the natural log of 2):  

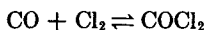
$$(k)(\text{half-life}) = kt_{1/2} = 0.693$$
  - Calculate a value for  $k$  for the reaction described in Fig. 12-2; express  $k$  in appropriate units.
  - Using the calculated value of  $k$  and the data in Table 12-2, calculate the rate  $R$  of the described reaction at times of 1 hr, 3 hr 33 min, and 12 hr 31 min; express  $R$  in appropriate units.
- The reaction of nitric oxide with water vapor is endothermic. In establishing the following equilibrium



suppose that 4 moles of nitric oxide and 6 moles of water vapor are introduced into a container and that the temperature is held at 500°C and the pressure at 10 atm till equilibrium is attained.

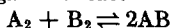
- With the information given, can the amount of each substance in the equilibrium mixture be calculated? Explain.
- Now if the temperature is increased to 600°C ( $P$  held constant), how will the relative amounts in the new equilibrium mixture compare with those at 500°C?
- If the temperature is maintained at 500°C but the mixture is permitted to expand till the pressure is decreased to 1 atm, how will the relative amounts at equilibrium compare with those when the system was at 500°C and 10 atm?

- d. How will the value of  $K$  for the equilibrium at  $500^{\circ}\text{C}$  compare with  $K$  at  $600^{\circ}\text{C}$ ?
- e. How will the value of  $K$  for the system at  $500^{\circ}\text{C}$  and 10 atm compare with  $K$  for the system at  $500^{\circ}\text{C}$  and 1 atm?
12. The equilibrium constants for three different reactions are  $1.3 \times 10^4$ ,  $2.6 \times 10^{-21}$ , and  $4.7 \times 10^6$ . Assuming that each reaction can be represented in the form  $A + B \rightleftharpoons C + D$ , for which of the three will the equilibrium mixture be more completely in the form of just two substances?
13. To produce phosgene, chlorine and carbon monoxide can be introduced into a reaction vessel in equal molar amounts and left at a specific temperature till equilibrium is attained. The gaseous equilibrium system is represented as follows:



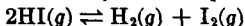
In an experiment carried out in a 500-ml flask, an analysis of the equilibrium mixture revealed there were 0.40 mole of phosgene, 0.15 mole of carbon monoxide, and 0.15 mole of chlorine.

- a. Calculate the equilibrium constant at this temperature.
  - b. How many moles of carbon monoxide were introduced into the flask initially?
14. In a second experiment (see Exercise 13), more carbon monoxide than chlorine was introduced. At equilibrium the mixture was found to contain 0.40 mole of phosgene and three times as much carbon monoxide as chlorine. Calculate the number of moles of carbon monoxide at equilibrium in the 500-ml vessel. (Use as much information from Exercise 13 as you need.)
15. If the equilibrium described in Exercise 13 is established in the presence of a catalyst, how will the relative proportions of chlorine, carbon monoxide, and phosgene be affected? How will the value of  $K$  be affected?
16. Consider the hypothetical gaseous reaction



If, at equilibrium, half of the material is present as equal amounts of  $\text{A}_2$  and  $\text{B}_2$  and half is present as  $\text{AB}$ , calculate the equilibrium constant  $K_p$ . (To make a typical calculation, one can assume a total pressure of 1 atm, 100 atm, or something convenient.)

17. At equilibrium at  $1000^{\circ}\text{C}$  hydrogen iodide is 33 per cent dissociated into hydrogen and iodine. Calculate  $K_p$  for the equilibrium



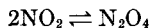
18. Consider this equilibrium system:



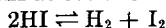
- a. If you were manufacturing ethene ( $\text{C}_2\text{H}_4$ ) from ethane ( $\text{C}_2\text{H}_6$ ), would you attempt to carry out the reaction at a low temperature or a high temperature? Why?
  - b. Would you use a low pressure or a high pressure? Explain why.
19. a. For the following gaseous equilibrium, how will the pressure of  $\text{NO}_2$  be affected if the pressure of the system is reduced so that the pressure

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of  $\text{N}_2\text{O}_4$  under a new equilibrium condition is one-third of its original value:



- b. Repeat (a) for the case in which the pressure of  $\text{N}_2\text{O}_4$  in the second equilibrium mixture is ten times its initial pressure.
20. Consider the gaseous equilibrium  $\text{A} \rightleftharpoons 2\text{B}$ . Suppose that 1 mole of A is put in a liter flask. If 0.8 mole of A is present when equilibrium is attained, calculate  $K$ .
21. The equilibrium constant for  $2\text{HCl} \rightleftharpoons \text{H}_2 + \text{Cl}_2$  at  $25^\circ\text{C}$  is extremely small.
- a. In an equilibrium mixture of hydrogen chloride, hydrogen, and chlorine at  $25^\circ$ , is the relative amount of HCl large or small?
- b. It is found that, when hydrogen and chlorine are mixed at  $25^\circ$  and allowed to stand (in the dark), the rate at which hydrogen chloride forms is very slow. Is this consistent with your answer to (a)? Explain.
22. a. How, if at all, will the relative amounts be changed when the pressure is increased for a high-temperature gaseous equilibrium system containing hydrogen, oxygen, and water vapor?
- b. Given that the decomposition of water into the elements is endothermic, how will temperature changes affect the relative amounts present in equilibrium mixtures?
- c. Write the expression for  $K$ .
- d. How will the value of  $K$  be affected by temperature changes?
23. Even though the rate of a reaction appears to be zero, for example,  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$  at room temperature, we do not like to say it is zero. Explain, using Fig. 12-4 as a guide.
24. A substance is held at  $25^\circ\text{C}$ . What can be said about the "temperature" of the individual molecules?
25. What is meant by "energy-rich molecules"?
26. A. H. Taylor and R. H. Crist, *J. Am. Chem. Soc.*, **63**, 1377 (1941), experimentally determined the concentrations of hydrogen, iodine, and hydrogen iodide in equilibrium mixtures obtained by starting with different concentrations of HI at  $393.7^\circ\text{C}$ :



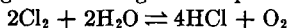
The results of two experiments are given below. For each set of data calculate the value of  $K$ . Is  $K$  the same for each experiment? (The concentrations are in moles per liter.)

	$\text{H}_2$	$\text{I}_2$	HI
experiment 1	0.46981	0.07014	1.3997
experiment 2	0.07106	0.07106	0.5468

27. The reaction  $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$  is extremely slow in the absence of a catalyst. Suggest a mechanism to explain the fact that platinum metal is a catalyst for this reaction.
28. The gas phase reaction  $2\text{H}_2\text{O} + 2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{SO}_4$  is catalyzed by a mixture of the gaseous oxides NO and  $\text{NO}_2$ . What sort of mechanism may account for this?

29. Distinguish between adsorption and absorption.

30. Consider the following exothermic gaseous equilibrium:

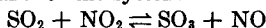


- a. How will an increase in pressure affect the amount of HCl at equilibrium?
- b. How will an increase of pressure affect the value of  $K_p$ ?
- c. How will a change in temperature affect the value of  $K_p$ ?

31. a. Calculate values of  $K_p$  for the reaction  $3\text{H}_2 + \text{N}_2 \rightleftharpoons 2\text{NH}_3$  at 400° and 10 atm; at 400° and 1,000 atm; at 500° and 10 atm; and at 500° and 1,000 atm.

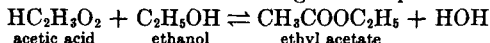
b. Compare the values calculated in (a) with the three values for  $K_p$  calculated in the text, and discuss the "constancy" of  $K_p$ .

32. The equilibrium constant for the system



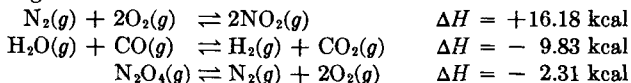
is 5 at a certain temperature. An equilibrium mixture at that temperature was found by analysis to contain 0.6 mole of  $\text{SO}_2$ , 0.3 mole of  $\text{NO}_2$ , and 1.1 moles of  $\text{SO}_3$  in a liter. Calculate the moles of NO per liter.

33. Acetic acid and ethanol react according to the equation



A good way to follow this equilibrium analytically is to determine the amount of acid that remains by titrating the mixture with a standard base. Suppose that 0.100 mole of acetic acid was mixed with 0.100 mole of ethanol and permitted to remain at constant temperature till equilibrium was attained. Thirty-three milliliters of 1.00 N sodium hydroxide was required to titrate the acetic acid remaining in the equilibrium mixture. Calculate  $K$ . (Note that volumes were not given. Because there are the same number of molecules in reactants and products, volume terms cancel.)

34. Consider the following reactions; the enthalpy change is for the reaction to the right as written:



- a. Write the expression for the equilibrium constant for each.
- b. For each predict the effect of an increase in pressure on the relative amounts of substances to the right and to the left of the arrows.
- c. Repeat (b) for the effect of an increase in temperature.
- d. For each of the reactions, predict the effect of adding  $\text{O}_2$  gas on concentrations of individual reactants at equilibrium.
- e. For each predict the effect of a decrease in temperature on the relative rates of reaction to the right and to the left, as written.
- f. For each predict the effect on equilibrium concentrations of adding a catalyst.

35. a. Equal volumes of  $\text{SO}_2$  and  $\text{NO}_2$  are introduced into a 3.00-liter steel vessel. The temperature is then increased to 827°C, and the mixture is held at this temperature till equilibrium is reached. (See equation in Exercise 32). If at equilibrium the mixture contains 0.961 mole of NO

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- and the total pressure is 9.00 atm at 827°C, what is  $K$  for the equilibrium? (Note: First calculate the total number of moles of gases that must be present in a 3.00-liter vessel to give a pressure of 9 atm at 827°C.
- b. How much  $\text{SO}_2$  must be added to the mixture in order to increase the amount of  $\text{NO}$  to 0.100 mole,  $T$  remaining at 827°C?
36. In the equilibrium mixture of nitrogen tetroxide and nitrogen dioxide,  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ , at 0°C and 1 atm, the partial pressures are  $\text{N}_2\text{O}_4$ , 0.8 atm;  $\text{NO}_2$ , 0.2 atm.
- a. Calculate the equilibrium constant  $K_p$  in terms of pressure units.
- b. Calculate the equilibrium constant  $K$  in terms of moles per liter. (Remember that 1 liter of a pure gas at 1 atm at 0°C contains 1/22.4 mole.)
- c. Is  $K_p$  numerically equal to  $K$ ?
- d. If equilibrium constants are to have meaning, we must be consistent with respect to certain conventions. State two.
37. The value of  $K$  for the reaction in Exercise 33 is 4.
- a. Calculate the moles of ethyl acetate there will be at equilibrium if 5 moles of acetic acid is initially added to 5 moles of ethanol.
- b. Repeat (a) assuming that 1 mole of acid and 3 of alcohol are initially mixed.

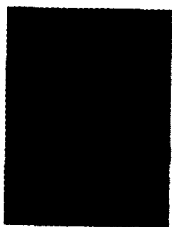
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# IONIC EQUILIBRIA

## IN SOLUTION



In our study of chemical equilibria in the previous chapter we devoted our attention mainly to processes involving molecules. The concept of equilibrium is of equal importance in understanding reactions involving ions, particularly in solution. In this chapter we shall apply the theories of equilibria to solutions of electrolytes in water.

We have previously noted (in Chap. 5) that ions in solution arise in two ways: (1) the solute is a truly ionic compound or salt, so that the ions simply separate in solution, or (2) the solute is a covalent or partially covalent compound that reacts with the solvent (for example, water) to form ions. The latter process is spoken of as an *ionization reaction*.

In case (1) the resulting solution is a strong electrolyte, with the solute considered to be 100 per cent in the form of solvated ions. In case (2) the solution can be a strong or a weak electrolyte, depending on the degree of ionization for the particular reaction. We first take up one of the important classes of weak electrolytes in water—the weak acids.

### IONIZATION OF WEAK ACIDS

Acids are classified as **monoprotic**, **diprotic**, **triprotic**, etc., depending on the number of protons (positive hydrogen ions) that can be donated per molecule. The equations for the ionization in water of some weak, monoprotic acids are as follows.<sup>1</sup>

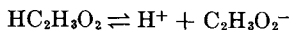
<sup>1</sup> In Chap. 5 it was pointed out that sometimes it is desirable to accent the interaction of  $H^+$  ions and  $H_2O$  molecules by using the hydronium ion,  $H_3O^+$ , in equations. In the present chapter we shall use  $H_3O^+$  whenever it contributes to a better understanding of the subject matter, especially when we wish to emphasize the attraction between protons and water molecules.

## IONIC EQUILIBRIA IN SOLUTION



FIG. 13-1

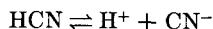
acetic acid



formic acid



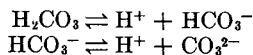
hydrocyanic acid



A carbonated beverage affords a good example of equilibria involving molecules and ions.

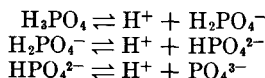
The ionization of a diprotic acid proceeds in two steps; Fig. 13-1 illustrates a well-known example of such equilibria:

carbonic acid



The ionization of a triprotic acid takes place in three steps:

phosphoric acid



## IONIZATION CONSTANTS

An equilibrium between ions and molecules can be treated mathematically in the same fashion as an equilibrium in which all species are molecules. The equilibrium constant for an ionization reaction is called the **ionization constant** ( $K_i$ ).

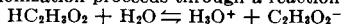
For the ionization of acetic acid, the expression for the ionization constant follows from the equation

$$\text{HC}_2\text{H}_3\text{O}_2 \rightleftharpoons \text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^-$$

as<sup>1</sup>

$$K_i = \frac{[\text{H}^+] \times [\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \quad (1)$$

<sup>1</sup> It is important to note that this ionization constant is actually the product of two constants, because the ionization proceeds through a reaction with water:



The usual expression for the equilibrium constant in the case above is

$$K = \frac{[\text{H}_3\text{O}^+] \times [\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2] \times [\text{H}_2\text{O}]}$$

However, the concentration of water remains practically unchanged in dilute acetic acid solutions of differing concentrations because of the relatively large amount of water present. So we may regard  $[\text{H}_2\text{O}]$  as constant when we are dealing with solutions of moderate concentration and write

$$K = \frac{[\text{H}_3\text{O}^+] \times [\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2] \times k}$$

$$\text{Then } K \times k = \frac{[\text{H}_3\text{O}^+] \times [\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

Or, because the product of two constants is constant,

$$K_i = \frac{[\text{H}_3\text{O}^+] \times [\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \quad (2)$$

Because the ionization of a diprotic acid proceeds in two steps, such acids have two ionization constants, one for each step. For the ionization of carbonic acid, these constants are defined as follows:

$$K_{i_1} = \frac{[H^+] \times [HCO_3^-]}{[H_2CO_3]}$$

$$K_{i_2} = \frac{[H^+] \times [CO_3^{2-}]}{[HCO_3^-]}$$

In a solution of a diprotic acid, the concentration of ions formed in the first step is much greater than in the second. Usually the numerical value of  $K_{i_1}$  is about  $10^4$  times that of  $K_{i_2}$ . The same ratio holds for the steps in ionization of a triprotic acid.

It is important to note that both steps in the ionization of a diprotic acid are taking place in the same solution. In a solution of  $H_2CO_3$  there is only one  $[H^+]$  concentration and only one  $[HCO_3^-]$  concentration. The same numerical values for these concentrations are used in calculating either  $K_{i_1}$  or  $K_{i_2}$ .

## DETERMINATION OF IONIZATION CONSTANTS

In order to calculate the ionization constant of a weak electrolyte, we must in some way determine the number of ions present in solution and the number of molecules of the electrolyte that are not ionized. One method of determining the concentration of ions is by measuring changes in colligative properties (see example of acetic acid in Table 10-3). Another way is by measuring the electrical conductivity—the greater the degree of ionization of a dissolved electrolyte, the greater the electrical conductivity of its solutions.

The amount of the electrolyte present as molecules is calculated by subtracting from the total amount of solute the amount that is determined to be present as ions. If our electrical measurements indicate that 5.2 per cent of the solute is present as ions, we assume that 94.8 per cent of the solute molecules are not ionized.

Measurement of the electrical conductance of 0.1  $M$  acetic acid reveals that it is 1.34 per cent ionized. In other words, when 0.1 mole of hydrogen acetate is dissolved in enough water to make 1 liter of acetic acid solution, ionization proceeds rapidly to equilibrium, with the result that 1.34 per cent of the hydrogen acetate is in the form of ions, and 98.66 per cent is in the form of covalent molecules. Of course, hydrogen acetate molecules ionize continually, but the hydrogen and acetate ions also reunite continually; both reactions take place at the same speed, so that the concentrations of ions and mole-

(Continued)

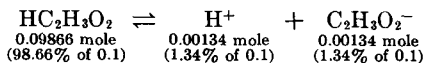
Note that the numerical value of  $K_i$  for Eq. (1) which contains  $[H^+]$ , must be the same as that for Eq. (2), which contains  $[H_3O^+]$ , because  $[H^+]$  and  $[H_3O^+]$  have the same value. At present, it is largely a matter of choice as to whether the expression for  $K_i$  for acids is written as in (1), where the proton is not shown attached to a water molecule, or as in (2), where the proton is shown attached to a simple water molecule.



## IONIC EQUILIBRIA IN SOLUTION

cules remain constant indefinitely, unless some change is made in the system.

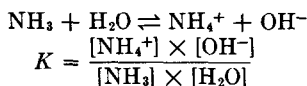
Using these data, we can calculate  $K_i$  for the ionization of 0.1 *M* acetic acid. The concentrations in moles per liter are



Placing the concentrations in the expression for the equilibrium constant and solving, we obtain

$$\begin{aligned} K_i &= \frac{0.00134 \times 0.00134}{0.09866} \\ K_i &= 1.82 \times 10^{-5} \end{aligned}$$

The ionization constants for weak bases are obtained in similar fashion. In the case of ammonium hydroxide



With solutions of moderate concentration, the amount of water remains constant for all practical purposes, and

$$\begin{aligned} K &= \frac{[\text{NH}_4^+] \times [\text{OH}^-]}{[\text{NH}_3] \times k} \\ K \times k &= \frac{[\text{NH}_4^+] \times [\text{OH}^-]}{[\text{NH}_3]} \end{aligned}$$

The product  $K \times k$  is the ionization constant  $K_i$ :

$$K_i = \frac{[\text{NH}_4^+] \times [\text{OH}^-]}{[\text{NH}_3]}$$

The ionization constant for ammonium hydroxide as calculated from conductance measurements is  $1.8 \times 10^{-5}$ . (The fact that it is numerically so nearly the same as that for acetic acid is just a coincidence.) Ionization constants for several weak electrolytes are given in Table 13-1. The magnitude of the constant is indicative of the tendency of the electrolyte to form ions; the smaller the constant, the less this tendency. Several arbitrary ranges of  $K_i$  values are used to describe acids or bases. One is given below:

very strong	$K_i$ greater than $1 \times 10^3$
strong	$K_i$ in range of $1 \times 10^3$ to $1 \times 10^{-2}$
weak	$K_i$ in range of $1 \times 10^{-2}$ to $1 \times 10^{-7}$
very weak	$K_i$ less than $1 \times 10^{-7}$

## Ionization constants of acids and bases at 25°C

TABLE 13-1

name	ionization reaction	$K_i$
hydrochloric acid	$\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$	large
sulfuric acid	$\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$	large
	$\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	$1.2 \times 10^{-2}$
sulfurous acid	$\text{H}_2\text{SO}_3 \rightleftharpoons \text{H}^+ + \text{HSO}_3^-$	$1.5 \times 10^{-2}$
	$\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-}$	$1.0 \times 10^{-7}$
phosphoric acid	$\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-$	$7.5 \times 10^{-3}$
	$\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}$	$6.2 \times 10^{-8}$
	$\text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-}$	$2.2 \times 10^{-13}$
hydrofluoric acid	$\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$	$6.7 \times 10^{-4}$
formic acid	$\text{HCHO}_2 \rightleftharpoons \text{H}^+ + \text{CHO}_2^-$	$1.8 \times 10^{-4}$
acetic acid	$\text{HC}_2\text{H}_3\text{O}_2 \rightleftharpoons \text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^-$	$1.8 \times 10^{-5}$
carbonic acid	$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	$4.3 \times 10^{-7}$
	$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	$5.6 \times 10^{-11}$
hydrocyanic acid	$\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^-$	$4.9 \times 10^{-10}$
zinc hydroxide	$\text{Zn(OH)}_2 \rightleftharpoons \text{ZnOH}^+ + \text{OH}^-$	$9.6 \times 10^{-4}$
methyl ammonium hydroxide (methyl amine in water)	$\text{CH}_3\text{NH}_2 \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^-$	$4.4 \times 10^{-4}$
ammonium hydroxide	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	$1.8 \times 10^{-5}$
urea	$\text{CON}_2\text{H}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CON}_2\text{H}_5^+ + \text{OH}^-$	$1.5 \times 10^{-14}$

**Calculation Involving  $K_i$ .** Once the constant for a given equilibrium is known, the constant can be used in making calculations that involve different concentrations. The following problem is an example, and several other examples are given in later sections of this chapter.

**PROBLEM 1** Given  $K_i$  for acetic acid as  $1.8 \times 10^{-5}$ , calculate the percentage of ionization of 0.50 *M* acetic acid.

**Solution** Let  $x$  = number of moles of  $\text{HC}_2\text{H}_3\text{O}_2$  ionized per liter.

Then  $x$  = moles of  $\text{H}^+$  ions and of  $\text{C}_2\text{H}_3\text{O}_2^-$  ions per liter. (The small amount of  $\text{H}^+$  ions due to ionization of the water itself is insignificant.)

And  $0.50 - x$  = moles of  $\text{HC}_2\text{H}_3\text{O}_2$  molecules per liter.

At equilibrium

$$\frac{[\text{H}^+] \times [\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.8 \times 10^{-5}$$

$$\frac{x \cdot x}{0.50 - x} = 1.8 \times 10^{-5}$$

To simplify the calculation, we can say that  $0.50 - x$  approximately equals 0.50, because acetic acid is a weak acid. Of the original 0.50 mole dissolved to make the solution, only a tiny fraction that here is represented as  $x$  has changed to ions.

$$1.8 \times 10^{-5} \approx \frac{x \cdot x}{0.50}$$

$$x^2 \approx 0.90 \times 10^{-5} = 9.0 \times 10^{-6}$$

$$x \approx \sqrt{9.0} \times \sqrt{10^{-6}}$$

$$\approx 3.0 \times 10^{-3} \text{ mole of acetic acid ionized}$$

$$\begin{aligned}\text{percentage of ionization} &= \frac{\text{no. of moles ionized}}{\text{total no. of moles of solute}} \times 100 \\ &\simeq \frac{3.0 \times 10^{-3}}{0.50} \times 100 \\ &\simeq 0.60 \text{ per cent}\end{aligned}$$

Comparing this result with the data given previously for the 0.1 *M* solution of acetic acid illustrates a general rule of great importance: *A dilute solution of a weak electrolyte is more completely ionized than a more concentrated solution.* The 0.1 *M* solution was 1.34 per cent ionized, whereas the much stronger 0.50 *M* solution was only 0.60 per cent ionized.

**APPROXIMATE CALCULATION VERSUS PRECISE CALCULATION.** When an expression such as  $0.50 - x$  or  $0.50 + x$  appears in a calculation, one can neglect  $x$  and make an approximate calculation, provided  $x$  is small compared with the figure subtracted from or added to. In the foregoing calculation,  $x$  turned out to be 0.003, which is small compared with 0.50, so that we conclude that we were justified in saying  $0.50 - x \simeq 0.50$ . To prove that neglecting  $x$  changes the answer in this problem hardly at all, we can carry out the calculation precisely:

$$\begin{aligned}\frac{x \cdot x}{0.50 - x} &= 1.8 \times 10^{-5} \\ x^2 &= 1.8 \times 10^{-5} \times (0.50 - x) \\ x^2 + 1.8 \times 10^{-5} x - 9 \times 10^{-6} &= 0\end{aligned}$$

We can solve this equation with the quadratic formula:

$$\begin{aligned}x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ x &= \frac{-1.8 \times 10^{-5} + \sqrt{(1.8 \times 10^{-5})^2 - 4(1)(-9 \times 10^{-6})}}{2(1)} \\ &= \frac{-1.8 \times 10^{-5} + \sqrt{36.0003 \times 10^{-6}}}{2} \\ &= \frac{5.98 \times 10^{-3}}{2} = 2.99 \times 10^{-3}\end{aligned}$$

The data justify only two significant figures in the answer, so that we round to  $x = 3.0 \times 10^{-3}$ . This is the same result that we got by saying  $0.50 - x \simeq 0.50$  and avoiding the use of the quadratic equation.

## DILUTION OF SOLUTIONS OF WEAK ELECTROLYTES

The addition of water to a weak electrolyte increases the extent of ionization. This can be easily demonstrated experimentally with the "cut wire" apparatus described in Chap. 5. When the wires are immersed in concentrated acetic acid, the electric bulb does not light; with moderate dilution, a faint glow appears; with further dilution, the light burns more brightly.

Immediately on diluting acetic acid with water, the forming of ions proceeds at a faster rate than the uniting of ions. In time the two rates become equal, and the system is at equilibrium. (Compare with Fig. 12-1.)

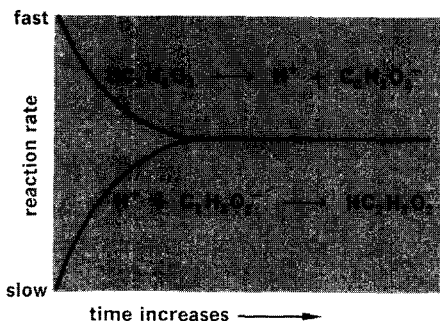
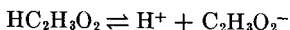


FIG. 13-2

The increase in ionization with dilution can be understood from examination of the reaction rates for the ionization of acetic acid:



At equilibrium for 0.100 *M* acetic acid (1.34 per cent ionized):

$$\begin{aligned} R_f &= k \times [\text{HC}_2\text{H}_3\text{O}_2] \\ &= k \times 0.09866 \\ R_r &= k' \times [\text{H}^+] \times [\text{C}_2\text{H}_3\text{O}_2^-] \\ &= k' \times 0.00134 \times 0.00134 \end{aligned}$$

Immediately after diluting to twice the original volume (a 0.050 *M* solution results):

$$\begin{aligned} R_f &= k \times \frac{1}{2} \times 0.09866 \\ R_r &= k' \times \frac{1}{2} \times 0.00134 \times \frac{1}{2} \times 0.00134 \end{aligned}$$

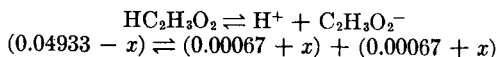
This means that, while the rate at which ions form was reduced to *one-half* by dilution, the rate at which covalent molecules form was reduced to *one-fourth* of its original value. Therefore, the system will not be at equilibrium immediately after dilution. However, because the ions are forming at a faster rate than they are recombining, they accumulate in the solution. In time, the concentration of the hydrogen and acetate ions will have increased, and the concentration of the hydrogen acetate molecules will have decreased, so that the rates of the two reactions will again be equal (Fig. 13-2). When this happens, the value of the ionization constant  $K_i$  will be the same as before,  $1.82 \times 10^{-5}$ , but the percentage of ionization will have increased.

**CALCULATION OF CONCENTRATIONS AFTER DILUTION.** To calculate concentrations at equilibrium after dilution, the method is as follows. Immediately on diluting to one-half of the original concentration,

$$[\text{HC}_2\text{H}_3\text{O}_2] = \frac{1}{2}(0.09866) = 0.04933 \text{ mole/liter}$$

$$\text{and } [\text{H}^+] = [\text{C}_2\text{H}_3\text{O}_2^-] = \frac{1}{2}(0.00134) = 0.00067 \text{ mole/liter}$$

To establish the new equilibrium condition, an amount  $x$  of the  $\text{HC}_2\text{H}_3\text{O}_2$  must ionize. The new equilibrium condition will be



Putting these concentrations into the equilibrium expression, we obtain

$$K_i = 1.8 \times 10^{-5} = \frac{(0.00067 + x) \times (0.00067 + x)}{(0.04933 - x)}$$

By cross multiplication and rearrangement we can obtain a quadratic equation and solve to find  $x = 0.00027$ .

Thus, at equilibrium  $[\text{HC}_2\text{H}_3\text{O}_2] = 0.04906$ , and the concentration of each of the ions is  $0.00094$  mole/liter. The percentage of ionization at this dilution is  $\left(\frac{0.00094}{0.50}\right) 100 = 1.9$  per cent, compared with 1.34 per cent before dilution. This is another calculation that shows that the more dilute a weak electrolyte is, the more ionized it must be if  $K_i$  is to remain constant.

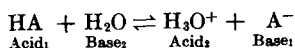
We have considered three different concentrations of acetic acid. Let us compare them by writing the expression of  $K_i$  for each:

concentration	0.50 M	0.10 M	0.050 M
$K_i$	$\frac{(0.0030)^2}{(0.497)}$	$\frac{(0.00134)^2}{(0.0987)}$	$\frac{(0.00094)^2}{(0.0491)}$

Each of these fractions must equal  $1.8 \times 10^{-5}$  if our calculations are correct, for we used the second fraction to calculate the constant ( $1.8 \times 10^{-5}$ ) and then used the constant to calculate the other two. However, our calculations show why the percentage of ionization must change on diluting a weak electrolyte if  $K_i$  is to remain constant (and we have an abundance of experimental evidence to indicate that it does). This behavior is similar to what we found in Chap. 12 for changes in relative amounts of reactants and products for equilibria involving different numbers of moles of reactants and products.

## GENERAL ACID-BASE RELATIONSHIPS

According to the Brønsted-Lowry definition<sup>1</sup> (Chap. 5) acids are *proton donors* and bases are *proton acceptors* (see Fig. 13-3). Because donating protons is a reversible reaction, every acid must form a base on donating its proton, and every base must form an acid on accepting a proton. For water systems, this relationship may be expressed in a general way:



The base that results when an acid donates its proton is called the conjugate base of the acid.  $\text{A}^-$  is the conjugate base of  $\text{HA}$ , and  $\text{H}_2\text{O}$

<sup>1</sup> Another concept of acids and bases is based on the Lewis definitions. Lewis defined an acid as any species that acts as an electron-pair acceptor in chemical reactions; a base acts as an electron-pair donor.

is the conjugate base of  $\text{H}_3\text{O}^+$ . Or  $\text{HA}$  is the conjugate acid of base  $\text{A}^-$ , and  $\text{H}_3\text{O}^+$  is the conjugate acid of the base  $\text{H}_2\text{O}$ . The following equations provide specific examples of this relationship:

acid <sub>1</sub>		base <sub>2</sub>		acid <sub>2</sub>		base <sub>1</sub>
$\text{HCl}$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	+	$\text{Cl}^-$
$\text{H}_2\text{O}$	+	$\text{NH}_3$	$\rightleftharpoons$	$\text{NH}_4^+$	+	$\text{OH}^-$
$\text{H}_2\text{O}$	+	$\text{CO}_3^{2-}$	$\rightleftharpoons$	$\text{HCO}_3^-$	+	$\text{OH}^-$
$\text{H}_3\text{O}^+$	+	$\text{C}_2\text{H}_3\text{O}_2^-$	$\rightleftharpoons$	$\text{HC}_2\text{H}_3\text{O}_2$	+	$\text{H}_2\text{O}$
$\text{H}_3\text{O}^+$	+	$\text{OH}^-$	$\rightleftharpoons$	$\text{H}_2\text{O}$	+	$\text{H}_2\text{O}$

Base<sub>1</sub> is the conjugate base of acid<sub>1</sub>; base<sub>2</sub> is the conjugate base of acid<sub>2</sub>.

**Strength of Acids and Bases.** An acid that has a great tendency to give up a proton is called a strong acid, and a base that has a great tendency to take up a proton is called a strong base.

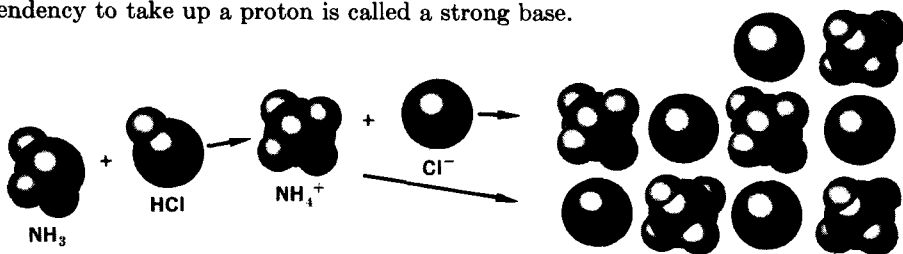
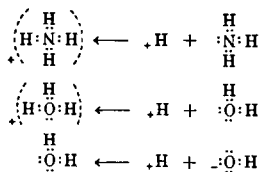


FIG. 13-3

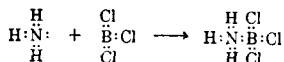
The two invisible gases,  $\text{HCl}$  and  $\text{NH}_3$ , combine on contact to form a white solid, ammonium chloride. In this reaction, a proton is transferred from the hydrogen chloride molecule (the acid) to an ammonia molecule (the base). The resulting chloride and ammonium ions then aggregate to form small crystals of the ionic compound, ammonium chloride,  $\text{NH}_4\text{Cl}$ . (See also Fig. 5-6.)

(Continued)

According to the Lewis definition, unsolvated protons act as electron-pair acceptors (acids) when reacting with hydroxide ion, water, or ammonia:



This definition, however, extends the concept of the acid-base relationship to a number of reactions not normally classed in this way. For example, in the following reaction, ammonia acts as a base and boron trichloride acts as an acid:



One advantage of the Lewis concept is that it identifies as acids certain nonhydrogen-containing substances that have the same function in chemical reactions as the common acids have.

# IONIC EQUILIBRIA IN SOLUTION

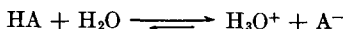
The conjugate base of a weak acid is a strong base. For example, water is a very weak acid; its conjugate base, the hydroxide ion,  $\text{OH}^-$ , is a very strong base, for it has a strong attraction for a proton. The  $\text{CO}_3^{2-}$  ion is a very strong base; therefore,  $\text{HCO}_3^-$  is a very weak acid.

The conjugate base of a strong acid is a weak base. The chloride ion, the conjugate base of hydrochloric acid, displays little tendency to react with protons to form hydrogen chloride molecules and hence is a weak base. Table 13-2 ranks several acids and bases in the order of comparative strength.

TABLE 13-2 *Relative strengths of acids and bases*

acid		conjugate base	
$\text{HClO}_4$	strong acids	$\text{ClO}_4^-$	weak bases
$\text{HCl}$		$\text{Cl}^-$	
$\text{HNO}_3$		$\text{NO}_3^-$	
$\text{H}_2\text{SO}_4$		$\text{HSO}_4^-$	
$\text{H}_3\text{O}^+$		$\text{H}_2\text{O}$	
$\text{H}_2\text{SO}_3$		$\text{HSO}_3^-$	
$\text{HSO}_4^-$		$\text{SO}_4^{2-}$	
$\text{H}_3\text{PO}_4$		$\text{H}_2\text{PO}_4^-$	
$\text{HC}_2\text{H}_3\text{O}_2$		$\text{C}_2\text{H}_3\text{O}_2^-$	
$\text{H}_2\text{CO}_3$		$\text{HCO}_3^-$	
$\text{H}_2\text{S}$	decreasing strength	$\text{HS}^-$	increasing strength
$\text{HSO}_3^-$	weak acids	$\text{SO}_3^{2-}$	strong bases
$\text{HCN}$		$\text{CN}^-$	
$\text{NH}_4^+$		$\text{NH}_3$	
$\text{HCO}_3^-$		$\text{CO}_3^{2-}$	
$\text{HS}^-$		$\text{S}^{2-}$	
$\text{H}_2\text{O}$		$\text{OH}^-$	
$\text{OH}^-$		$\text{O}^{2-}$	
$\text{NH}_3$		$\text{NH}_2^-$	

**Leveling Effect.** Each of the acids listed in Table 13-2 has an *intrinsic acidity* defined by its tendency to donate a proton. In certain solvents, for example, it is easily shown that  $\text{HClO}_4$  is a stronger acid than  $\text{HNO}_3$ . However, in water solutions all the acids listed in Table 13-2 as stronger than  $\text{H}_3\text{O}^+$  are of practically the same strength. For any very strong acid,  $\text{HA}$ , the ionization in water

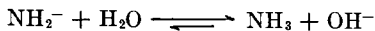


goes essentially to completion. This means that  $\text{H}_3\text{O}^+$  is the strongest acid that can exist in a significant amount in water solution.

The reaction of a solvent to reduce a number of different reagents to the same strength is called the **leveling effect**. The strongest Brønsted acid that can exist in a solvent is the *onium ion* of that solvent.

Water also has a leveling effect on any potential base that has an intrinsic basicity greater than  $\text{OH}^-$ . If sodium amide,  $\text{NaNH}_2$ , con-

tacts water, the following reaction takes place (as we would predict from Table 13-2):

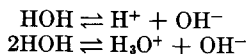


The very strong base  $\text{NH}_2^-$  cannot exist in water solution; nor can  $\text{O}^{2-}$ . Both these strong proton acceptors are leveled to form solutions of the strongest base that can exist in water, the  $\text{OH}^-$  ion.

Other solvents also level the strengths of potential acids and bases. In liquid ammonia acids stronger than  $\text{NH}_4^+$  are leveled to the strength of  $\text{NH}_4^+$  (the onium ion in ammonia). The strongest base in ammonia is the amide ion,  $\text{NH}_2^-$ . The strongest base possible in the solvent liquid hydrogen sulfate,  $\text{H}_2\text{SO}_4$ , is the  $\text{HSO}_4^-$  ion.

## IONIZATION OF WATER

Electrical conductance measurements and other evidence show that water ionizes to a limited extent in accordance with the following equation:



or

The tendency for water to ionize is very slight as compared with the tendency for the reverse reaction (neutralization) to occur. Consequently, at equilibrium the relative number of ions is very small.

Precise measurement of the electrical conductance of very pure water at  $25^\circ\text{C}$  reveals that its ionic composition is as follows:

$$\begin{aligned} [\text{H}^+] &= 1 \times 10^{-7} \text{ mole/liter} \\ [\text{OH}^-] &= 1 \times 10^{-7} \text{ mole/liter} \end{aligned}$$

At  $25^\circ$ , there are 55.35 moles of water in 1 liter. Hence only 1 out of every 553,500,000 water molecules is ionized, an amount so insignificant that we probably would not bother to mention the ionization of water if we were dealing only with pure water. However, we shall be much concerned with this equilibrium and with the changes in ionic concentration when substances are dissolved in water. To begin with, the expression for the equilibrium constant for the ionization of water,

$$K_i = \frac{[\text{H}^+] \times [\text{OH}^-]}{[\text{HOH}]}$$

can be modified to the extent that the concentration of water molecules is considered to be constant.

The change of a million billion molecules of water into ions, or vice versa, does not produce a detectable change in the enormous number of water molecules in a liter of water, but it does produce a large change in the number of ions. Considering that  $[\text{HOH}]$  remains constant at 55.35 moles/liter, we may write

$$K_i = \frac{[\text{H}^+] \times [\text{OH}^-]}{55.35}$$



Then

$$K_i \times 55.35 = [\text{H}^+] \times [\text{OH}^-]$$

Or because the product of two constants is also a constant, we may write

$$K_w = [\text{H}^+] \times [\text{OH}^-]$$

By substituting the hydrogen ion and hydroxide ion concentrations in this expression, we can calculate the value of the constant:

$$\begin{aligned} K_w &= 1 \times 10^{-7} \times 1 \times 10^{-7} \\ &= 1 \times 10^{-14} \end{aligned}$$

This constant,  $K_w$ , is called the **ion product for water**. It indicates that in pure water or in any water solution both hydrogen and hydroxyl ions must be present and, moreover, that the product of their concentrations must be constant. It may seem odd, but acid solutions contain a small concentration of hydroxide ions (base), and basic solutions contain a small concentration of hydrogen ions (acid). Further, if the concentration of one of these ions is known, the other can be easily calculated, because the product of the two must equal  $1 \times 10^{-14}$  ( $K_w$  at  $25^\circ$ ).<sup>1</sup>

For example, if hydrogen chloride, HCl, is added to water till the solution contains  $1 \times 10^{-4}$  mole/liter of the  $\text{H}^+$  ion, the  $\text{OH}^-$  ion concentration is calculated as follows:

$$\begin{aligned} K_w &= [\text{H}^+] \times [\text{OH}^-] \\ 1 \times 10^{-14} &= 1 \times 10^{-4} \times [\text{OH}^-] \\ [\text{OH}^-] &= \frac{1 \times 10^{-14}}{1 \times 10^{-4}} \\ &= 1 \times 10^{-10} \text{ mole/liter} \end{aligned}$$

Conversely, if sodium hydroxide,  $\text{Na}^+$ ,  $\text{OH}^-$ , is added to water till the solution is 0.001 molar ( $1 \times 10^{-3}$ ), the hydrogen ion concentration can be calculated in this way:

$$\begin{aligned} 1 \times 10^{-14} &= [\text{H}^+] \times 1 \times 10^{-3} \\ [\text{H}^+] &= \frac{1 \times 10^{-14}}{1 \times 10^{-3}} \\ &= 1 \times 10^{-11} \text{ mole/liter} \end{aligned}$$

## EXPRESSING HYDROGEN ION CONCENTRATION

In water solutions, common acidic properties are due to hydrogen ions, and common basic properties to hydroxide ions. If the concentration of the hydrogen ions is greater than  $1 \times 10^{-7}$  mole/liter, the solution is said to be acidic; if the concentration is less than this, the solution is basic. Because the product of the concentrations of these two ions is constant ( $1 \times 10^{-14}$ ), it is necessary to state the concen-

<sup>1</sup>The value of  $K_w$  increases slightly as the temperature rises. For ordinary purposes, the value is taken as  $1 \times 10^{-14}$  when the temperature is at or near room temperature.

tration of only one in order to describe the extent of the acidity or alkalinity of the solution. A widely used method of stating the hydrogen ion concentration of dilute acids, bases, and neutral solutions is in terms of  $pH$ . The  $pH$  of a solution is defined as follows:

$$pH = \log \frac{1}{[H^+]}$$

or

$$pH = -\log [H^+]$$

The logarithm of a number is the power to which the number 10 must be raised to give the number. The logarithm of 10 is 1; of 100, 2; of 0.001, -3. A logarithm table is required to find the logarithm if the number is not an exact multiple (or submultiple) of 10. A table of logarithms is given in the Appendix. Four examples will illustrate the use of  $pH$ .

1. The hydrogen ion concentration of water is  $1 \times 10^{-7}$  mole/liter at  $25^\circ C$ . The  $pH$  of water is

$$pH = \log \frac{1}{1 \times 10^{-7}} = \log (1 \times 10^7) = \log 1 + \log 10^7 = 0 + 7 = 7$$

2. A solution of hydrochloric acid is 0.0063  $N$ . If we assume complete ionization, the hydrogen ion concentration is 0.0063 mole/liter. The  $pH$  of the solution is

$$pH = \log \frac{1}{0.0063} = \log (1.59 \times 10^2) = \log 1.59 + \log 10^2 = 2.2$$

Alternate calculation:

$$pH = -\log 0.0063 = -(\bar{3}.80) = -(-3 + 0.80) = 2.2$$

3. A solution of  $NaOH$  is 0.01  $N$ . The  $OH^-$  ion concentration follows from the definition of a normal solution as 0.01, or  $1 \times 10^{-2}$  mole/liter. Before calculating the  $pH$ , we must obtain the hydrogen ion concentration:

$$\begin{aligned} K_w &= [H^+] \times [OH^-] \\ 1 \times 10^{-14} &= [H^+] \times 1 \times 10^{-2} \\ [H^+] &= \frac{1 \times 10^{-14}}{1 \times 10^{-2}} = 1 \times 10^{-12} \text{ mole/liter} \end{aligned}$$

We then obtain the  $pH$  in the usual manner:

$$pH = \log \frac{1}{[H^+]} = \log \frac{1}{1 \times 10^{-12}} = \log (1 \times 10^{12}) = 12$$

For some purposes it is convenient to focus attention on the  $[OH^-]$  and to speak of the  $pOH$ , the negative logarithm of  $[OH^-]$ . This 0.01  $N$  solution of  $NaOH$  has a  $pOH$  of 2. The sum of  $pOH$  and  $pH$  for the same solution is 14.

## IONIC EQUILIBRIA IN SOLUTION

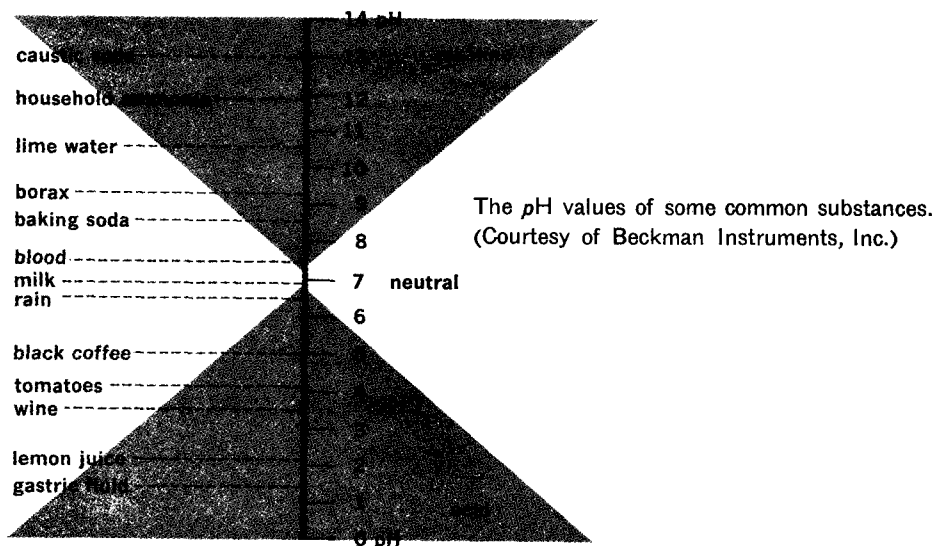


FIG. 13-4

4. A solution of ammonium hydroxide is 0.01 *N*. Although this solution has the same normality as the sodium hydroxide solution above, and potentially as much base is present, the  $\text{OH}^-$  ion concentration is much less than 0.01, because ammonium hydroxide is a weak base; that is, much of it is present as covalent molecules. Obtaining the equilibrium constant from Table 13-1, we can proceed with calculating the  $\text{OH}^-$  ion concentration in the equilibrium mixture:

$$\begin{aligned} \text{NH}_3 + \text{HOH} &\rightleftharpoons \text{NH}_4^+ + \text{OH}^- \\ 0.01 - x \text{ mole/liter} &\quad x \text{ mole/liter} \quad x \text{ mole/liter} \\ K_i &= \frac{[\text{NH}_4^+] \times [\text{OH}^-]}{[\text{NH}_3]} \\ 1.8 \times 10^{-5} &= \frac{x \cdot x}{0.01 - x} \\ 1.8 \times 10^{-5} &\simeq \frac{x \cdot x}{0.01} \\ x &\simeq 4 \times 10^{-4} \text{ mole/liter concentration of } \text{OH}^- \text{ ion} \end{aligned}$$

From this point the calculations are similar to those above for 0.01 *N* NaOH:

$$\begin{aligned} K_w &= [\text{H}^+] \times [\text{OH}^-] \\ 1 \times 10^{-14} &\simeq [\text{H}^+] \times 4 \times 10^{-4} \\ [\text{H}^+] &\simeq \frac{1 \times 10^{-14}}{4 \times 10^{-4}} \\ &\simeq 0.25 \times 10^{-10} \text{ mole/liter} \\ \text{pH} &\simeq \log \frac{1}{0.25 \times 10^{-10}} = \log \left( \frac{1}{0.25} \times 10^{10} \right) = \log (4 \times 10^{10}) \\ &\simeq \log 4 + \log 10^{10} = 0.6 + 10 = 10.6 \end{aligned}$$

From the foregoing examples we see that, if the *pH* is 7, the solution is neutral; if the *pH* is below 7, the solution is acidic; if the *pH* is

above 7, the solution is basic. Figure 13-4 shows  $pH$  values for some common substances.

## INDICATORS

The accurate determination of the hydrogen ion concentration, or the  $pH$ , of a solution involves methods that cannot be discussed here. An approximate measurement can be made readily with **indicators**. Indicators are usually complex organic compounds that are one color if the hydrogen ion concentration is above a certain value and a different color if it is lower. The particular  $pH$  at which the color change occurs depends on the indicator. By using a variety of indicators and noting their colors in the solution, we can arrive at a fair estimate of the acidity or basicity of soils, water, body fluids, and other types of solutions. Seven of these useful substances are listed in Table 13-3, but many others are available.

### Indicators

TABLE 13-3

name	$pH$ at which color change occurs	acid color	base color
methyl yellow	2-3	red	yellow
methyl orange	3-4.5	red	yellow
sodium alizarin sulfate	4.5-6.5	yellow	violet
litmus	6-8	red	blue
phenolphthalein	8-10	colorless	red
thymolphthalein	10-12	yellow	violet
trinitrobenzene	12-13	colorless	orange

## HYDROLYSIS

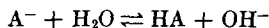
Water solutions of normal salts may be neutral, acidic, or basic, depending on the salt. An aqueous solution of ammonium chloride,  $NH_4Cl$ , turns blue litmus red; a sodium carbonate solution,  $Na_2CO_3$ , has the opposite effect. An aqueous solution of sodium chloride,  $NaCl$ , has no effect on litmus.

In order to account for these differences, we must consider the possibility of the ions of the salt reacting with water. When the cation or the anion (or both) of a salt reacts with water so as to change the  $pH$ , the salt is said to be **hydrolyzed**; the reaction is referred to as **hydrolysis**. These reactions involve the transfer of protons and as such are a special type of protolysis reaction.

Four important possibilities are to be considered when a normal salt is dissolved in water.

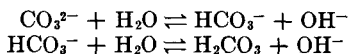
1. *The anion of the salt acts as a base.* Suppose a water solution is made of a salt that contains an anion that is a fairly strong proton

acceptor. These anions remove protons from the water and thereby increase the concentration of  $\text{OH}^-$  ions:



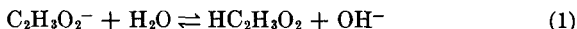
$K_w$  must remain constant at  $1 \times 10^{-14}$ .

When equilibrium is established, the concentration of the hydroxide ion will have risen to a value greater than that for pure water (more than  $1 \times 10^{-7}$  mole/liter), and the concentration of the hydrogen ion will have fallen to a value less than that for water (less than  $1 \times 10^{-7}$ ). Therefore, the water solution of such a salt is basic. By referring to Table 13-2, we see that the carbonate ion,  $\text{CO}_3^{2-}$ , the sulfide ion,  $\text{S}^{2-}$ , and the acetate ion,  $\text{C}_2\text{H}_3\text{O}_2^-$ , are among the ions that are classed as fairly strong bases. Salts containing these ions tend to form basic solutions, assuming that the positive ions of the salt are not strong acids. Specific examples are sodium carbonate,  $\text{Na}_2\text{CO}_3$ , potassium carbonate,  $\text{K}_2\text{CO}_3$ , sodium acetate,  $\text{NaC}_2\text{H}_3\text{O}_2$ , calcium acetate,  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ , barium acetate,  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ , sodium sulfide,  $\text{Na}_2\text{S}$ , and potassium sulfide,  $\text{K}_2\text{S}$ . All of these are ionic compounds; and in each case, when the salt is dissolved in water, the anion reacts to a certain extent with hydrogen ions from the water. For sodium carbonate, the reactions are



At equilibrium, the concentrations will have become adjusted in a manner that satisfies the ionization constant for carbonic acid and the ion product constant for water. However, because the carbonate and bicarbonate ions have reacted with water to form hydroxide ions, the concentration of the hydroxide ion is more than  $1 \times 10^{-7}$  mole/liter, and the concentration of the hydrogen ion is less than  $1 \times 10^{-7}$  mole/liter. The pH of this solution is more than 7; that is, the solution is basic.

The equilibrium for a water solution of calcium acetate is



Again, the pH of the solution is more than 7 because of the formation of hydroxide ions by the reaction of water molecules and acetate ions. The water solution of calcium acetate is basic.

2. *The cation of the salt acts as an acid.* The ammonium ion,  $\text{NH}_4^+$ , the hydrated copper(II) ion,  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ , and the hydrated iron(III) ion,  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ , can give up protons and can therefore act as weak acids. A water solution of a salt containing one of these ions is acidic, provided the anion of the salt does not have a strong tendency to react with protons. (Examples of such anions are  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ . See Table 13-2 for other suitable weakly basic anions.) Some of the salts that hydrolyze to give acidic solutions are ammonium chloride,  $\text{NH}_4\text{Cl}$ , ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , ammonium sulfate,

In solutions of copper chloride, copper nitrate, and copper sulfate, protons are donated by hydrated copper ions to water molecules. When equilibrium is reached, the solutions have a higher concentration of  $\text{H}_3\text{O}^+$  ions than pure water has and so are acidic.

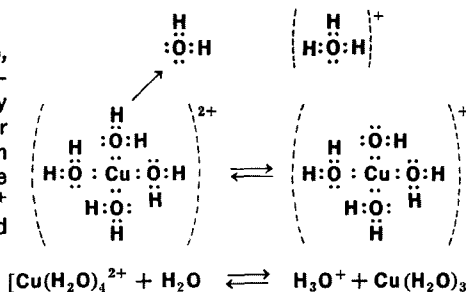
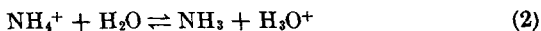


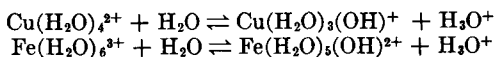
FIG. 13-5

$(\text{NH}_4)_2\text{SO}_4$ , copper(II) chloride,  $\text{CuCl}_2$ , copper(II) nitrate,  $\text{Cu}(\text{NO}_3)_2$ , and iron(III) chloride,  $\text{FeCl}_3$ .

For ammonium chloride, the equilibrium that becomes established in a water solution and has a significant effect on the concentrations of hydrogen and hydroxide ions is



The ammonium ion, a weak acid, donates a proton to a water molecule, a weak base. As the hydronium ion concentration rises, the hydroxide ion concentration falls. Most ammonium salts form solutions that have pH values of less than 7. For hydrated ions, such as  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$  and  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ , the reactions are



In the hydrates of small, highly charged metal ions, the attraction of the positive metal ion for electrons tends to weaken the covalent bond between oxygen and hydrogen, with the result that nearby water molecules are able to remove a certain percentage of the loosely bonded protons (see Fig. 13-5).

3. *The anion can act as a base and the cation as an acid.* The salt, ammonium acetate,  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ , is composed of a cation,  $\text{NH}_4^+$ , that can function as a weak acid, and an anion,  $\text{C}_2\text{H}_3\text{O}_2^-$ , that can function as a weak base. A water solution of this salt is essentially neutral, because the formation of  $\text{OH}^-$  ions by the reaction of water with the acetate ions—see Eq. (1) above—is just balanced by the formation of  $\text{H}_3\text{O}^+$  ions by the reaction of water with the ammonium ions—Eq. (2). The pH of the solution is about 7, and the solution is neutral to litmus.

A water solution of ammonium carbonate, however, is basic, because the carbonate ions react with water to form  $\text{OH}^-$  ions to a greater extent than the  $\text{NH}_4^+$  ions react to form  $\text{H}_3\text{O}^+$  ions.

4. *Neither the anion nor the cation acts as a base or an acid.* Salts composed of cations from the strongly electropositive metals ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Sr}^{2+}$ ) and anions from strong acids ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) form neutral solutions. Examples are sodium chloride,  $\text{NaCl}$ ,

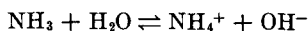
potassium chloride, KCl, barium chloride, BaCl<sub>2</sub>, calcium chloride, CaCl<sub>2</sub>, sodium nitrate, NaNO<sub>3</sub>, sodium sulfate, Na<sub>2</sub>SO<sub>4</sub>, and calcium nitrate Ca(NO<sub>3</sub>)<sub>2</sub>.

A water solution of sodium chloride is neutral (pH 7). That is, the sodium ions do not react with water to form H<sup>+</sup> ions, nor do the chloride ions react appreciably with water molecules to form OH<sup>-</sup> ions.

### COMMON ION EFFECT

The ionization of a weak electrolyte is markedly decreased by adding to the solution an ionic compound containing one of the ions of the weak electrolyte. This effect is called the **common ion effect**.

Let us illustrate this by considering a water solution of ammonia. The following equilibrium exists in such a solution:



When solid ammonium chloride (NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>) is added to this solution, the concentration of NH<sub>4</sub><sup>+</sup> ions is greatly increased. The rate of the reverse reaction is therefore increased greatly, whereas the rate of the forward reaction is unaffected at first. But as the ions are consumed by the faster reaction, the concentration of the undissociated molecules (NH<sub>3</sub>, H<sub>2</sub>O) increases, and the rate of the forward reaction begins to increase. In time, the two rates become equal again, and the equilibrium is reestablished. In the new equilibrium condition, the concentration of the NH<sub>4</sub><sup>+</sup> ions is greater than in the first equilibrium, and the concentration of the OH<sup>-</sup> ions is less. The value for *K<sub>i</sub>* will be the same for either equilibrium.

In the same manner, the ionization of weak acids is suppressed by the addition of the salts of these acids. A dilute solution of acetic acid contains a lower concentration of the hydrogen ion when sodium acetate is also present.

The foregoing examples illustrate a general rule: Weak acids and bases become even weaker in solutions with their salts.

**PROBLEM 2** Calculate the concentration of hydrogen ions in a solution that is 0.1 *M* with respect to acetic acid and 0.2 *M* with respect to NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>. Given: *K<sub>i</sub>* for acetic acid is 1.8 × 10<sup>-5</sup>.

*Solution* Because sodium acetate is a strong electrolyte (a salt) and because acetic acid is sparingly ionized, the amount of acetate ion present depends almost entirely on the concentration of sodium acetate:

$$[\text{C}_2\text{H}_3\text{O}_2^-] \simeq 0.2 \text{ mole/liter}$$

The concentration of hydrogen acetate molecules may be taken as approximately equal to the concentration of the acetic acid (very little is in the form of ions):

$$[\text{HC}_2\text{H}_3\text{O}_2] \simeq 0.1 \text{ mole/liter}$$

Now we can proceed with calculating the hydrogen ion concentration:

$$1.8 \times 10^{-5} = \frac{[\text{H}^+] \times [\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \simeq \frac{[\text{H}^+] \times 0.2}{0.1}$$

$$[H^{+}] \approx \frac{1.8 \times 10^{-5} \times 0.1}{0.2} \approx \frac{1.8 \times 10^{-5} \times 1 \times 10^{-1}}{2 \times 10^{-1}}$$

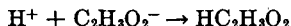
$$\approx 0.9 \times 10^{-5} \text{ or } 9 \times 10^{-6} \text{ mole/liter}$$

Note (page 333) that the concentration of  $H^{+}$  ions in 0.1 *M* acetic acid (no salt is present) is  $1.3 \times 10^{-3}$  mole/liter, over a hundred times greater than when sodium acetate is present to the extent of 0.2 *M*.

## BUFFERED SOLUTIONS

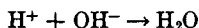
A solution that contains a weak acid plus a salt of that acid or a weak base plus a salt of that base has the ability to react with both acids and bases. Such a system is referred to as a **buffered solution**, because small additions of either acids or bases produce little change in the *pH*. Buffered solutions are of importance in many natural and synthetic systems.

For example, if more acid is added to a solution containing acetic acid and sodium acetate, the acetate ions react with the added hydrogen ions to form neutral hydrogen acetate molecules:

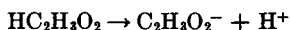


The *pH* does not appreciably change.

On the other hand, if hydrogen ions are removed by the addition of a base,



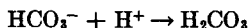
the molecular hydrogen acetate ionizes to form more hydrogen ions:



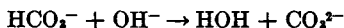
Again, the *pH* of the solution does not change significantly unless large quantities of the base are added.

In the blood, carbonic acid and sodium bicarbonate act as one buffer system to help maintain the *pH* of blood at a constant value (close to 7.4), even though acidic and basic substances continually pass into the blood stream. The buffer action in this case is vital, for if the *pH* increases or decreases by a small amount, death may result. A solution containing bicarbonate ions may act as a buffer, as is apparent from the following equations.

When an acid is added,



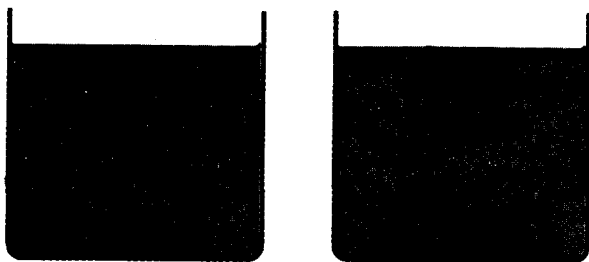
When a base is added,



A substance that, like the bicarbonate ion, can act either as an acid or a base is said to be **amphoteric**. Any amphoteric species, molec-



## IONIC EQUILIBRIA IN SOLUTION



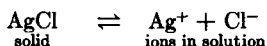
At a given temperature, saturated solutions of a salt contain the same ionic concentrations irrespective of the amount of undissolved salt present.

FIG. 13-6

ular or ionic, can act as a buffer. Most buffers, however, consist of a mixture of at least one acidic and at least one basic species. Buffer mixtures for establishing various  $pH$  ranges are listed in reference books.

### SOLUBILITY PRODUCT CONSTANT

When a saturated solution of a slightly soluble salt is in contact with undissolved salt, there is an equilibrium between the dissolved ions and the ions in the solid phase of the undissolved salt (see Fig. 13-6). For silver chloride, the equilibrium is formulated as follows:



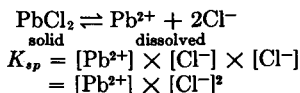
The equilibrium constant is given by the usual expression:

$$K = \frac{[\text{Ag}^+] \times [\text{Cl}^-]}{[\text{AgCl}]}$$

But at saturation, the concentration of the dissolved salt is not changed by adding more solid  $\text{AgCl}$ ; so that regardless of the amount of solid silver chloride present at saturation, the effect of the solid is constant:

$$\begin{aligned} K &= \frac{[\text{Ag}^+] \times [\text{Cl}^-]}{k} \\ K \times k &= [\text{Ag}^+] \times [\text{Cl}^-] \\ K_{sp} &= [\text{Ag}^+] \times [\text{Cl}^-] \end{aligned}$$

This constant,  $K_{sp}$ , is known as the **solubility product constant**. It is equal to the product of the ionic concentrations (in moles per liter of saturated solution), with each concentration raised to the power indicated by the number of ions in the formula. For example, the solubility product for  $\text{PbCl}_2$  is formulated as follows:



For  $\text{Ca}_3(\text{PO}_4)_2$ ,

$$K_{sp} = [\text{Ca}^{2+}]^3 \times [\text{PO}_4^{3-}]^2$$

**Calculation of Solubility Product Constants.** The solubility of silver chloride as experimentally determined is 0.0014 g/liter at 25°C. Because the molecular weight of silver chloride is 143.32, its solubility in moles per liter is  $0.0014 \div 143.32 = 0.000010 = 1.0 \times 10^{-5}$  mole/liter. Hence the concentration of the  $\text{Ag}^+$  ion is  $1.0 \times 10^{-5}$  mole/liter; the concentration of the  $\text{Cl}^-$  ion is also  $1.0 \times 10^{-5}$  mole/liter, because there is one  $\text{Cl}^-$  ion for each  $\text{Ag}^+$  ion. Substituting these values in the solubility product expression, we have

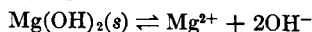
$$\begin{aligned} K_{sp} &= [\text{Ag}^+] \times [\text{Cl}^-] \\ &= 1.0 \times 10^{-5} \times 1.0 \times 10^{-5} \\ &= 1.0 \times 10^{-10} \end{aligned}$$

The solubility product constants for several salts are given in Table 3 in the Appendix. Solubility products are listed only for slightly soluble substances, because the  $K_{sp}$  relationship holds precisely only in dilute solutions.

**Calculation of Solubility from  $K_{sp}$  Value.** If we know the value of the solubility product constant, we can calculate the solubility of a salt.

**PROBLEM 3** Given that  $K_{sp}$  for  $\text{Mg}(\text{OH})_2$  is  $1.2 \times 10^{-11}$ , calculate the solubility of this compound in grams per 100 ml of solution.

**Solution** To see clearly the relationships of molar solubilities, we write the equation for the solubility equilibrium:



From the equation we see

(if  $x$  moles per liter of  $\text{Mg}(\text{OH})_2$  dissolves)  $\xrightarrow{\text{there is formed in solution}}$  ( $x$  moles  $\text{Mg}^{2+}$  per liter) + ( $2x$  moles  $\text{OH}^-$  per liter)

$$K_{sp} = [\text{Mg}^{2+}] [\text{OH}^-]^2$$

Letting  $x$  equal the moles of  $\text{Mg}(\text{OH})_2$  dissolved,

$$K_{sp} = (x)(2x)^2 = 4x^3$$

$$4x^3 = 1.2 \times 10^{-11}$$

$$x^3 = \frac{1.2 \times 10^{-11}}{4} = 3 \times 10^{-12}$$

$$x = 1.4 \times 10^{-4} \text{ mole/liter } \text{Mg}(\text{OH})_2 \text{ dissolved}^1$$

$$\begin{aligned} \text{solubility } \text{Mg}(\text{OH})_2 &= \frac{1.4 \times 10^{-4} \text{ mole}}{1 \text{ liter}} \times \frac{58.3 \text{ g}}{1 \text{ mole}} \times \frac{1 \text{ liter}}{1000 \text{ ml}} \times 100 \text{ ml} \\ &= 8.2 \times 10^{-4} \text{ g (in 100 ml of solution)} \end{aligned}$$

**Common Ion Effect in Precipitation.** In the foregoing examples of solubility product calculations, we have considered the salt to be dissolved in pure water. Generally, however, a solution contains an

<sup>1</sup> A convenient way to take the cube root of a number is with logarithms. The log of 3 is 0.4771. The log of the cube root of 3 is  $0.4771/3 = 0.1590$ . The antilog of 0.1590 is 1.443, which we round to 1.4.

## IONIC EQUILIBRIA IN SOLUTION

additional source of one of the ions of the insoluble salt. The influence that changing the concentration of one ion has on the concentration of the other ion is another instance of the common ion effect. For example, we calculated in Problem 3 that 1 liter of saturated  $\text{Mg}(\text{OH})_2$  contains  $1.4 \times 10^{-4}$  moles of  $\text{Mg}^{2+}$  ions. However, if the  $\text{OH}^-$  ion concentration is increased by adding a salt containing a common ion— $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Ca}(\text{OH})_2$ —the concentration of  $\text{Mg}^{2+}$  must decrease in order to keep  $K_{sp}$  constant; that is,  $\text{Mg}(\text{OH})_2$  is less soluble in a solution containing  $\text{NaOH}$  than in pure water.

As another example of the common ion effect, consider the precipitation of calcium carbonate. Suppose that, to a solution of sodium carbonate, some calcium chloride is added till the concentration of calcium ion in the solution becomes  $2 \times 10^{-3}$  mole/liter. What is the concentration of carbonate ion that can remain in solution? Calcium carbonate is generally thought of as being water-insoluble. Actually, it is soluble to the extent defined by its solubility product constant. At  $20^\circ\text{C}$ ,

$$K_{sp} = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] = 1 \times 10^{-8}$$

If  $[\text{Ca}^{2+}]$  is  $2 \times 10^{-3}$ , the value of  $\text{CO}_3^{2-}$  is easily calculated:

$$\begin{aligned} 2 \times 10^{-3} \times [\text{CO}_3^{2-}] &= 1 \times 10^{-8} \\ [\text{CO}_3^{2-}] &= \frac{1 \times 10^{-8}}{2 \times 10^{-3}} \\ [\text{CO}_3^{2-}] &= 5 \times 10^{-6} \text{ mole/liter} \end{aligned}$$

Our first conclusion is that only  $5 \times 10^{-6}$  mole/liter of carbonate ion can remain in solution at equilibrium if the concentration of calcium ion is  $2 \times 10^{-3}$  molar.

Another conclusion that we can draw is that, if the original sodium carbonate is extremely dilute (less than  $5 \times 10^{-6} M$ ), no calcium carbonate precipitate forms when calcium ion is added to make  $[\text{Ca}^{2+}]$  equal to  $2 \times 10^{-3}$ . Suppose  $[\text{CO}_3^{2-}]$  had been only  $3 \times 10^{-6}$ :

$$[\text{Ca}^{2+}][\text{CO}_3^{2-}] = 2 \times 10^{-3} \times 3 \times 10^{-6} = 6 \times 10^{-9}$$

which is less than  $1 \times 10^{-8}$ , the value of  $K_{sp}$ . If substitution of the ionic concentrations into the expression for the solubility product leads to a calculated value less than the  $K_{sp}$  for the salt, no precipitate forms.

It is clear from a consideration of the solubility product principle that an ion cannot be completely removed from solution by forming a so-called insoluble precipitate with another ion. However, the addition of a large excess of the latter ion decreases the concentration of the former ion to the vanishing point (see Fig. 13-7). In the precipitation of  $\text{CO}_3^{2-}$  ion by the addition of  $\text{Ca}^{2+}$  ion, if calcium ion is added to the solution till its concentration is  $0.5 M$ , the concentration of the

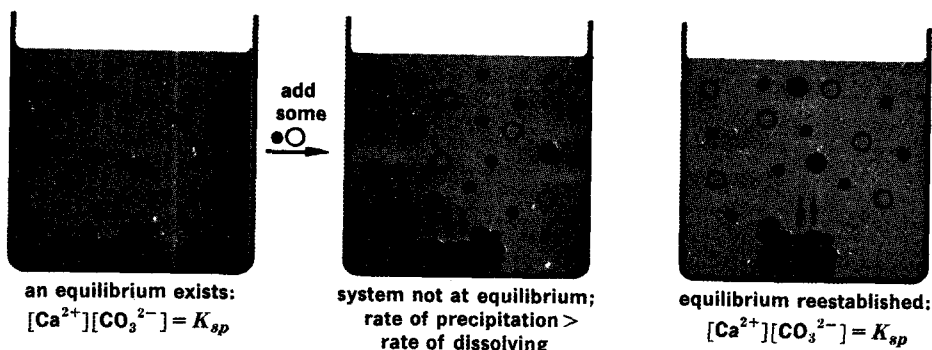


FIG. 13-7

When a salt containing calcium ions (represented as black spheres) is added to a saturated solution of calcium carbonate (black and blue spheres), the concentration of the  $Ca^{2+}$  ion is increased and the system is no longer at equilibrium (beaker 2). In time, the concentrations of  $Ca^{2+}$  and  $CO_3^{2-}$  are reduced by precipitation and the system is again at equilibrium (beaker 3). Note that in the new equilibrium system (beaker 3), the concentration of  $CO_3^{2-}$  is less and the concentration of  $Ca^{2+}$  is greater than in the original solution (beaker 1).

$CO_3^{2-}$  ion is reduced to only  $2 \times 10^{-8}$  mole/liter (that is, only 0.0000012 g of  $CO_3^{2-}$  per liter):

$$\begin{aligned} [Ca^{2+}] \times [CO_3^{2-}] &= 1 \times 10^{-8} \\ 0.5 \times [CO_3^{2-}] &= 1 \times 10^{-8} \\ [CO_3^{2-}] &= \frac{1 \times 10^{-8}}{0.5} = 2 \times 10^{-8} \text{ mole/liter} \end{aligned}$$

The decrease in solubility of a salt due to the presence of a common ion is made use of in analysis. To precipitate nearly all the silver ion in a solution as  $AgCl$ , we can add  $HCl$  to give a rather high  $[Cl^-]$  value. If  $[Cl^-] = 0.10$ ,  $[Ag^+] = 1.56 \times 10^{-9}$ , a very small amount left in solution. However, there can be a limit to the effect of a common ion. In concentrated  $HCl$  solutions, silver forms the soluble ion  $AgCl_2^-$  and  $AgCl$  dissolves. As mentioned previously, the solubility product concept applies only in dilute solution.

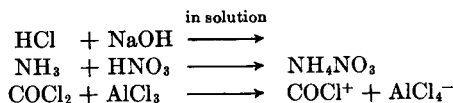
## CHAPTER REVIEW

### Terms

Ionization reaction, strong and weak electrolytes, monoprotic, diprotic, triprotic, ionization constant,  $K_i$ , percentage of ionization, Brønsted-Lowry acid and base, proton donors and acceptors, conjugate acid and base, Lewis acid and base, strong and weak acids and bases, leveling effect, ion product of water,  $K_w$ , pH, indicators, hydrolysis, common ion effect, buffered solutions, solubility product constant,  $K_{sp}$ , qualitative analysis.

### Exercises

1. Illustrate two different processes that give rise to ionic solutions. Write balanced equations for three examples of each process.
2. Write the equations for all the theoretical steps in the ionizations of the following:
  - a. Diprotic  $\text{H}_2\text{SO}_4$
  - b. Monobasic  $\text{NH}_4\text{OH}$
  - c. Triprotic  $\text{H}_3\text{AsO}_3$
  - d. Monoprotic  $\text{HC}_3\text{H}_5\text{O}_2$
  - e. Tribasic  $\text{Bi}(\text{OH})_3$
  - f. Diprotic  $\text{H}_3\text{PO}_4$
3. For each of the cases in Exercise 2 write the expression for the ionization constant for the step that involves the ion of highest charge.
4. The ionization constant is a special kind of equilibrium constant. Explain how it differs from the usual equilibrium constant  $K$ .
5. For the first ionization constant of sulfuric acid,  $\text{H}_2\text{SO}_4$ , show how the ionization constant is related to the equilibrium constant for the reaction with water to produce ions.
6. In a solution of 1  $M$  phosphoric acid,  $\text{H}_3\text{PO}_4$ , what ion is present in the greatest concentration and what in the smallest? Support your choice with chemical equations.
7. A monoprotic acid is found to be 8.0 per cent ionized at a concentration of 0.01000  $N$ . Calculate its ionization constant.
8. Using the data in Table 13-1, calculate the approximate percentage of ionization in 0.10  $N$  and in 0.0010  $N$  solutions of formic acid and hydrocyanic acid.
9. What is the conjugate base of hydrofluoric acid,  $\text{HF}$ ; of iodic acid,  $\text{HIO}_3$ ? Which of these bases is the stronger if the ionization constant of  $\text{HIO}_3$  is  $1.7 \times 10^{-1}$ ?
10. Analyze the following equations in terms of the Lewis definition of acids and bases:



11. Analyze the following reactions in solution in terms of the Brønsted-Lowry definition and write acid-base reactions; in the case of salts, indicate the ions that are present initially:
 
$$\begin{array}{lcl}
 \text{NaCN} + \text{HClO}_4 & \longrightarrow & \text{NH}_3 + \text{H}_2\text{CO}_3 \longrightarrow \\
 \text{NaHS} + \text{NaHSO}_4 & \longrightarrow & \text{HCN} + \text{HCl} \longrightarrow
 \end{array}$$
12. Explain why water solutions of  $\text{HCl}$  and  $\text{HClO}_4$  are practically equal in acid strength, even though  $\text{HClO}_4$  is known to be a much stronger acid under certain other circumstances.
13. a. Would solutions of the following salts act as acids or as bases when dissolved in liquid  $\text{HCN}$ :  
 $\text{NaNO}_3$ ,  $\text{NaOH}$ ,  $\text{NaCN}$ ,  $\text{NaCl}$ ,  $\text{NaNH}_2$ ?  
 b. Which solution would be the least basic? Illustrate your answer with an equation.



**IONIC EQUILIBRIA  
IN SOLUTION**

25. Explain in general terms the conditions under which a salt AB would be expected to hydrolyze. How could one determine if hydrolysis did take place or not? Might there be any case in which a simple measurement of the pH would not reveal if hydrolysis had taken place?
26. When salts are dissolved in water they may form acidic, neutral, or basic solutions. Write equilibrium equations to account for the following observations:  $\text{Na}_2\text{CO}_3$ , strongly basic;  $\text{KCl}$ , neutral;  $\text{NH}_4\text{NO}_3$ , slightly acidic;  $\text{KC}_2\text{H}_3\text{O}_2$ , slightly basic;  $\text{NaNO}_3$ , neutral.
27. Account, with an equation, for the fact that a solution of aluminium nitrate tastes sour.
28. How is the ionization of phosphoric acid affected when sodium phosphate,  $\text{Na}_3\text{PO}_4$ , is also present in a water solution? What is this effect called?
29. An aqueous solution of potassium fluoride plus hydrofluoric acid is described as a buffer solution, whereas a solution of potassium chloride plus hydrochloric acid is not. Explain with equations.
30. In 500 ml of 1.0 M acetic acid is dissolved 20.5 g of sodium acetate. What is the pH of the solution?
31. A small amount of hydrochloric acid is added to a solution that contains benzoic acid and sodium benzoate. (Benzoic acid,  $\text{HC}_7\text{H}_5\text{O}_2$ , is a monoprotic acid.  $K_i = 7 \times 10^{-5}$ .) (a) Write equations to show the changes that occur. (b) How will the pH of the solution be affected?  
A few drops of sodium hydroxide solution are now added. (c) Write equations to show the changes that occur. (d) How will the pH of the solution be affected? (e) The solution of benzoic acid and sodium benzoate is an example of what type of solution?
32. a. The  $K_i$  for aspirin (acetyl salicylic acid,  $\text{HC}_9\text{H}_7\text{O}_4$ ) is about  $1 \times 10^{-4}$ . Calculate the approximate pH of a 0.1 M aspirin solution that is also 0.1 M in sodium acetyl salicylate.  
b. Is the mixture referred to in (a) a buffered solution or not?  
c. What will be the immediate reactions of the mixture in (a) when it enters the stomach, based on the information in Exercise 23?
33. a. Write the equation for the hydrolysis of sodium acetate.  
b. Write the expression for the hydrolysis constant,  $K_h$ , for the hydrolysis reaction. If  $K$  is the equilibrium constant,  $K[\text{HOH}] = K_h$ .  
c. Show that  $K_h = K_w/K_i$ , where  $K_i$  is the ionization constant for acetic acid.  
d. Calculate a numerical value of  $K_h$ .  
e. For a 0.10 M solution of sodium acetate, calculate the molar concentrations of  $\text{OH}^-$  and  $\text{H}^+$  ions.
34. a. Calculate the pH of a 0.10 M solution of  $\text{NH}_4\text{Cl}$ . (Suggestion: See Exercise 33. Relate the hydrolysis constant for the hydrolysis reaction to the ionization constant for ammonium hydroxide and the ion product of water.)  
b. Calculate the pH of a 0.10 M solution of  $\text{NaCN}$ .
35. Two solutions are made, one by dissolving 0.1 mole of sodium carbonate in a liter of water, the other by dissolving 0.1 mole of sodium benzoate in

- a liter of water. Which solution is more basic? Formulate mathematical expressions whose solutions would lead to the hydrogen ion concentrations of each. (Refer to Exercise 31 and Table 13-1 for data.)
36. a. In overall terms, how will the hydrogen ion concentration in a liter of each of the following solutions be affected by the addition of 1 mole of solute ammonium chloride: 1 *N* KCl; 1 *N* KOH; 1 *N* HCl; and 1 *N* NH<sub>4</sub>OH?
  - b. Calculate the hydrogen ion concentration in each of the four solutions before and after the addition of the ammonium chloride.
  37. a. When 0.20 *N* sodium hydroxide is titrated with 0.20 *N* hydrochloric acid, what is the *pH* of the solution when the equivalent amount of acid has been added?
  - b. Repeat (a) for the titration of 0.20 *N* ammonium hydroxide with hydrochloric acid.
  - c. On the basis of (a) and (b), explain why different indicators are used for different acid-base titrations.
  38. Calculate the degree of hydrolysis (fraction in hydrolyzed form at equilibrium) of potassium cyanide in a 1.0 *M* solution. (See suggestion in Exercise 34.)
  39. a. A solution of ammonium acetate can act as a buffer. Explain, with equations.
  - b. A solution of potassium bicarbonate can act as a buffer. Explain, with equations.
  40. Using data from Table 3 in the Appendix, calculate the solubility in grams per liter of calcium sulfate, lead chloride, iron(III) hydroxide, and arsenic(III) sulfide.
  41. a. The solubility of BaCrO<sub>4</sub> is 0.00034 g per 100 ml of water. Calculate *K<sub>sp</sub>*.
  - b. The solubility of CaF<sub>2</sub> is 0.0016 g per 100 ml of water. Calculate *K<sub>sp</sub>*.
  42. a. How many moles per liter of dissolved Pb<sup>2+</sup> can there be in a liter of solution in which the sulfate ion concentration is 0.25 *M*?
  - b. Suppose lead sulfate were precipitated from a lead nitrate solution by adding sodium sulfate till the sulfate ion was 0.25 *M*. What weight of lead nitrate (in the form of its ions) would remain per liter of solution?
  43. a. Will a precipitate form if enough sodium sulfate is added to a 0.001 *M* solution of calcium nitrate to make the sulfate ion concentration 0.001 *M*?
  - b. Repeat (a) for the case in which sodium sulfate is added to a 0.001 *M* solution of lead nitrate.
  44. Calcium phosphate or copper sulfide is insoluble in water but more soluble in concentrated hydrochloric acid. Explain, with the aid of equations.

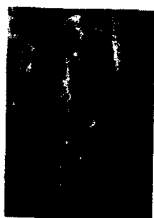


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# NUCLEAR REACTIONS



For several centuries, the alchemists

tried vainly to convert base metals into gold, a process that would have required the changing of one element into another (*transmutation*). About the beginning of the nineteenth century, scientists generally became convinced that elements were made of atoms that could not be converted one to another. Their conclusions were drawn from observation of ordinary chemical reactions and from interpretation of the laws that govern the weight relationships of these reactions.

For the next hundred years, the atom was thought of as a compact, impenetrable, indivisible object, perhaps spherical, that could be neither created nor destroyed. Then in 1896 came the discovery by Henri Becquerel in Paris that a compound of uranium, potassium uranyl sulfate, emitted a radiation that could pass through paper, or even thin sheets of metals, and affect a photographic plate. This discovery revived interest among scientists as to the internal structure of atoms and the possibility of the transmutation of elements, an interest that in sixty years led to the transmutation of most of the elements, the production of atomic bombs, the peacetime use of atomic energy, and a fuller (though still incomplete) understanding of the internal structure of atoms.

## RADIOACTIVE ELEMENTS

An element that undergoes spontaneous emission of radiations is said to be **radioactive**. Examples of naturally radioactive elements are radium, uranium, and polonium. Radioactive changes differ from ordinary chemical reactions in that the former involve transformations that originate in the nucleus of the atom, whereas ordinary chemical reactions involve changes in the outer-shell electrons only.

**Nuclides.** We have frequently used the term *isotopes* to refer to the atoms of a given element that have different masses. A broader and more inclusive term is *nuclides*. This term is used to refer to all the different kinds of atoms (about 1,700) of all the elements without regard to their atomic numbers or mass numbers. For example, the nuclides of hydrogen and oxygen include all the isotopes of hydrogen and all the isotopes of oxygen; or we speak of the "isotopes of zinc," but "the nuclides of mass numbers between 60 and 80."

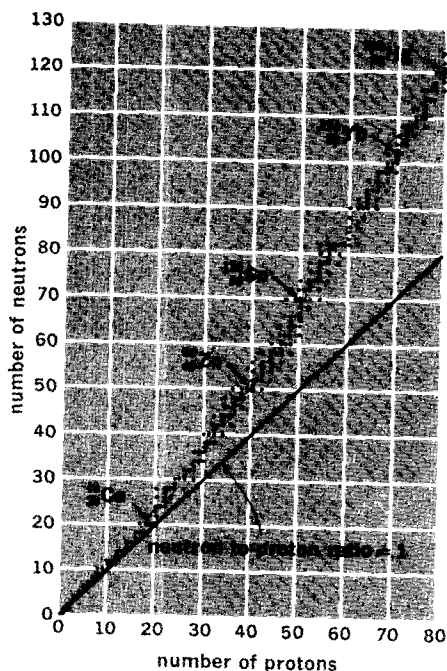
Nuclides are represented symbolically by placing the mass number as a left superscript and the atomic number as a left subscript. The known nuclides of hydrogen and helium, for example, are  ${}^1_1\text{H}$ ,  ${}^2_1\text{H}$ ,  ${}^3_1\text{H}$ ,  ${}^3_2\text{He}$ ,  ${}^4_2\text{He}$ , and  ${}^6_2\text{He}$ . Such a symbol is often used to designate not only a neutral atom, but its ion or even its nucleus. When desired, the charge, if any, can be shown as a right superscript in the usual manner, for example,  ${}^4_2\text{He}^{2+}$  to show a helium nucleus. This method of representation is the one recommended by the International Union of Chemistry and is used the world over with the exception of the United States, where many chemists place the mass number as a right superscript in the place where the charge is usually shown.

**Radioactive Decay.** As the result of a radioactive emission, a nuclide of one kind can change to a different nuclide. For example, the radioactive nuclide  ${}^{211}_{84}\text{Po}$  emits a particle and changes to  ${}^{207}_{82}\text{Pb}$ . Such a change is spoken of as a **radioactive decay**. Nuclides that undergo radioactive decay are said to be unstable; depending on the rate at which they decay, they can be said to be more or less unstable. Nuclides that are not radioactive are said to be stable.

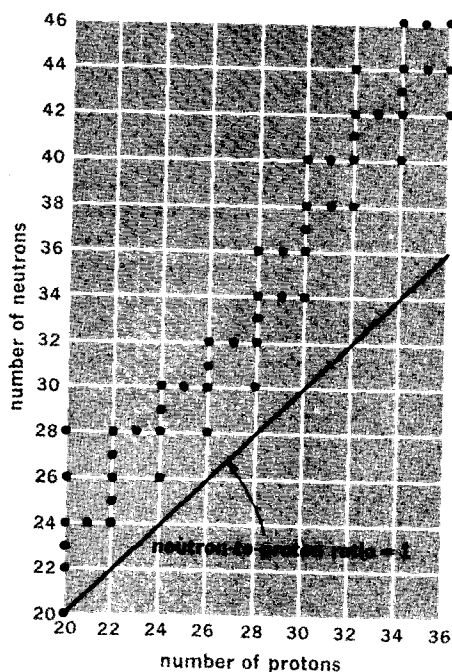
## NUCLEAR STABILITY

All known elements have two or more nuclides. In a few cases (aluminum is an example), only one nuclide occurs naturally, but synthetic nuclides of these elements have been produced by methods to be discussed later in the chapter. For elements with low and intermediate atomic numbers, most have both stable and unstable or radioactive nuclides. Consider hydrogen as an example. The nuclei of protium and deuterium atoms are stable, but those of tritium atoms are quite unstable; tritium decays so rapidly, in fact, that none would be found in nature if it were not being continually formed in very small amounts by natural nuclear changes. Both stable and unstable nuclides are known for all the common elements, such as sodium, oxygen, nitrogen, chlorine, carbon, potassium, silver, and so on, although many of the unstable nuclides do not occur appreciably, if at all, in nature.

In the case of elements with high atomic numbers, beginning with  ${}_{84}\text{Po}$ , no stable nuclides are known, although some nuclides are much



(a)



(b)

The increase of neutrons over protons as the atomic number increases is shown (a) for stable nuclides through atomic number 80. Note that the nuclide  $^{40}_{20}\text{Ca}$  is the largest atom with a neutron-proton ratio of 1. In (b), a portion of the data is replotted to a larger scale to show more clearly that stable nuclides with even numbers of either protons or neutrons are more numerous than those with odd numbers.

FIG. 14-1

more unstable than others; for example,  $^{223}_{88}\text{Ra}$  is more unstable than  $^{238}_{92}\text{U}$ .

Apparently one of the factors related to nuclear stability is a favorable **neutron-proton ratio**. Study Fig. 14-1. In this figure the number of protons is plotted against the number of neutrons for the stable nuclides. Note that, as the atomic number increases, the ratio of neutrons to protons increases; that is, neutrons become relatively more numerous in a given nucleus. For the nuclide  $^{12}_6\text{C}$ , the neutron-proton ratio is 6:6 or 1; for  $^{207}_{82}\text{Pb}$ , it is 125:82 or 1.53. That is, although the nuclei of carbon atoms contain an equal number of neutrons and protons, those of lead atoms have approximately 50 per cent more neutrons than protons. Each is stable. If the neutron-proton ratio of a nuclide lies outside the so-called favorable belt for nuclear stability, the nuclide is radioactive. Both  $^{210}_{82}\text{Pb}$  and  $^{14}_6\text{C}$  are radioactive. To provide for a more favorable neutron-proton ratio, radioactive nuclides emit particles and, in so doing, achieve a neutron-

proton ratio that provides for stability. Just how the neutron-proton ratio is changed by radioactive emission is discussed in the next section.

It is interesting to note that an even number of either protons or neutrons in the nucleus, except for the very light elements, is associated with a larger number of stable nuclides. For example, by consulting Fig. 14-1, it can be seen that there are five stable nuclides that contain 28 neutrons, four that contain 30 neutrons, and three that contain 32 neutrons, but only one stable nuclide that contains 29 neutrons, one that contains 31 neutrons, and one that contains 33 neutrons. The same kind of comparisons can be made for even and odd numbers of protons. For example, from the same figure we note that there are four stable isotopes of  $_{26}\text{Fe}$ , but only one of  $_{27}\text{Co}$ , five of  $_{28}\text{Ni}$ , but only two of  $_{29}\text{Cu}$ , and five of  $_{30}\text{Zn}$ , but only two of  $_{31}\text{Ga}$ . The three elements of intermediate atomic numbers that do not occur in nature, that is, do not have stable isotopes, have odd atomic numbers: technetium,  $_{43}\text{Tc}$ ; promethium,  $_{61}\text{Pm}$ ; and astatine,  $_{85}\text{At}$ .

From experimental observations and calculations of the binding energy of the nucleus (see page 369), it has been found that there is a special stability associated with nuclei having so-called *magic numbers* of either protons or neutrons. The magic numbers are 2, 8, 20, 50, 82, and 126. Especially stable are the nuclei having magic numbers of both protons and neutrons. Examples:  $^4_2\text{He}$ ,  $^{16}_8\text{O}$ ,  $^{40}_{20}\text{Ca}$ , and  $^{208}_{82}\text{Pb}$ . The word "magic" has been applied to these numbers to remind us that the mystery of their obvious importance has yet to be satisfactorily accounted for by any theory.

**Structure of the Nucleus.** In preceding chapters, the point has often been made that similarly charged particles, such as protons, repel one another. As a matter of fact, as two protons are brought closer together, the repulsion, known as *coulombic* or *electrostatic repulsion*, continues to increase. At distances less than about  $1 \times 10^{-13}$  cm the protons are thought to attract one another with a force greater than the electrostatic repulsion. We shall not attempt an explanation of these short-range attractive forces existing between nuclear particles except to say that other particles, for example, *mesons* and *pions*, are thought to be involved in them.

Aside from charge, most of the properties of protons and neutrons are very much alike. For example, they have approximately the same mass, and their short-range attraction for one another (proton for proton, neutron for neutron, or proton for neutron) are about the same. These facts have led to the idea that protons and neutrons may be different states of a single particle called the *nucleon*. We shall occasionally use this term to refer to either a neutron or proton in the nucleus of an atom.

Several models have been proposed recently to describe the organization of nucleons in atomic nuclei. One model, the *liquid drop model*,

Three kinds of natural radioactivity can be identified by determining the effect of a magnetic field on their paths of travel.

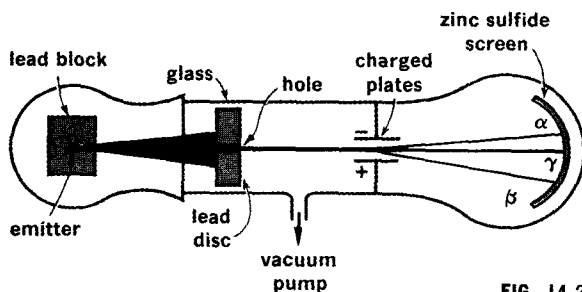


FIG. 14-2

is built on the resemblance of nuclear matter to a drop of liquid. A second one, the *Fermi gas model*, emphasizes the "free-particle" character of nucleons and thus relates the nucleons to a gas whose volume is the volume of the nucleus. A third model, the *shell model*, is particularly interesting to the student of general chemistry in that this model, among other things, suggests that the nucleons are arranged in energy levels just as are the electrons outside the nucleus. The magic numbers of 2, 8, 20, 28, 50, 82, and 126 are believed to be the number of neutrons or protons which fill shells or main levels. It might be pointed out that the theories of nuclear structure that we have simply mentioned have been developed rather extensively and are based on a great deal of experimental data.

## TYPES OF EMISSIONS

Figure 14-2 is a schematic diagram of an apparatus that can be used to show that a mixture of radioactive elements emits three kinds of radiations. The whole apparatus is enclosed in a vessel from which the air can be pumped, so that the emissions are not deflected by air molecules as they travel toward the photographic plate. A sample of radioactive material emits radiations in every direction. But if the emitters are placed inside a lead block that has a hole in it, only the radiations that are directed straight out the hole in the lead block escape and go through the slit in the metal shield. The emissions then travel in a straight line toward a photographic film unless acted on by some outside force, in this case a magnet. Without the magnet, only one spot, the image of the slit, is exposed on the photographic film, and it is directly in line with the position of the slit. However, when the emissions have to travel through a magnetic field (the magnet is shown in place in Fig. 14-2), three dark spots appear on the film; one of them is in line with the slit, and the other two are displaced above and below this spot. This experiment shows that one of the emissions is able to pass through a magnetic field without being deflected by the field. This one must be neutral in character. The other two spots represent the places where charged particles are striking after being deflected by the magnetic field; that is, a positive particle is deflected in one direction, a negative particle in the opposite direction. There-

fore this experiment shows three kinds of emissions: one positive, one negative, and one neutral.

These different emissions were shown to exist before they were completely understood, so that their discoverers named them simply alpha ( $\alpha$ ), beta ( $\beta$ ), and gamma ( $\gamma$ ). The characteristics of these three types of radioactivity are summarized in Table 14-1.

Whenever a sample of an element emits alpha or beta particles, atoms of another element are formed. This important observation leads to the inescapable conclusion that the alpha and beta particles come from the atomic nuclei of the radioactive substance. Beta radiation has been shown to be a stream of electrons traveling at a rate up to 95 per cent of the speed of light. Alpha radiation has been shown to be a stream of helium ions,  $\text{He}^{2+}$ . If a solid that emits alpha radiation is sealed in an evacuated glass tube, the tube gradually becomes filled with helium gas. This fact, coupled with the knowledge that an alpha particle has a charge of  $2+$  and a mass of about 4 awu, leads to the conclusion that the alpha particle is identical with the particle formed when a helium atom loses two electrons. Evidently, when a speeding alpha particle slows down sufficiently, it takes two electrons from some atom or ion it touches and thereby becomes a helium atom:

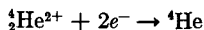


TABLE 14-1 *Natural radioactivity*

name	symbol	unit charge	mass, awu	typical velocity* relative to velocity of light, per cent	approximate* relative penetrating power	approximate* relative ionizing power	theoretical description
alpha particle	$\alpha$	$2+$	4	5	1	10,000	$\text{He}^{2+}$ ion
beta particle	$\beta$	$1-$	0.00055	95	100	100	an electron
gamma ray	$\gamma$	0	0	100	10,000	1	radiant energy

\*Given only for comparison.

When an atom emits either an alpha or a beta particle, it usually emits a gamma ray at the same time. The gamma rays emitted by the different radioactive substances have different energies and different penetrating power.

All three types of emissions are called **ionizing radiations**, because they are able to cause the formation of ions in matter by knocking electrons off the atoms or molecules in their path. The chief effects of radioactivity on living plants and animals are traceable to these ionization reactions.

## DETECTION OF RADIATIONS

Because atomic and subatomic particles cannot be seen and because radiant energy of short wavelength—that is, gamma rays—is not detectable by the eye, various indirect methods have been developed for detecting the emissions of radioactive substances. Four methods will be described. All are based on the fact that, as the emissions disturb atoms, electrons are displaced to higher energy levels.

**Photographic Methods.** Photographic film and paper have long been used for the detection of radioactivity. The emissions affect the photographic emulsion in the same manner as ordinary light does. After exposure, the paper or film is developed in the usual way.

**Fluorescent Methods.** Many substances are capable of receiving radiant energy of short wavelength (for example, gamma rays, X rays, ultraviolet rays), or of receiving kinetic energy from fast-moving particles (for example, beta and alpha particles) and transforming it into radiant energy of a wavelength that is in the region detectable by the eye. Substances that transform such energies into visible light are said to **fluoresce**. A common example of fluorescence is afforded by the luminous paint used on a watch dial. The paint ordinarily consists of 1 part of radium sulfate,  $\text{RaSO}_4$ , to 100,000 parts of zinc sulfide,  $\text{ZnS}$ . The invisible emissions of the radioactive radium atoms strike the zinc sulfide molecules, with the result that some of the energy is transformed into visible radiant energy.

A simple cloud chamber. An alpha emitter is glued onto the head of the pin in the cork. The cool area in the vicinity of the metal plate becomes supersaturated with methyl alcohol vapor, and the cloud tracks form here.

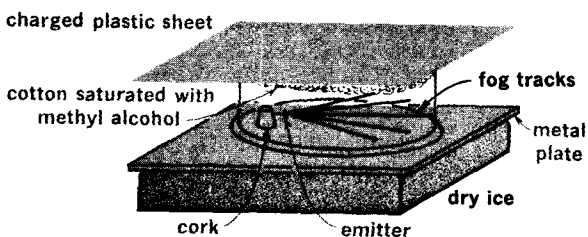


FIG. 14-3

**Cloud Chamber.** An apparatus perfected in 1911 by C. T. R. Wilson, an English physicist, made it possible to see the path followed by a single ionizing radiation in its flight through a gas. Wilson made artificial clouds in the laboratory by first saturating a volume of air with water vapor and then causing the moist air to cool by expanding it rapidly. If the cooling is sufficient, a cloud will form; if there is somewhat less cooling, the air will only become *supersaturated* with moisture. (Substances other than water—for example, an alcohol—can be used to supersaturate the air with vapor.)



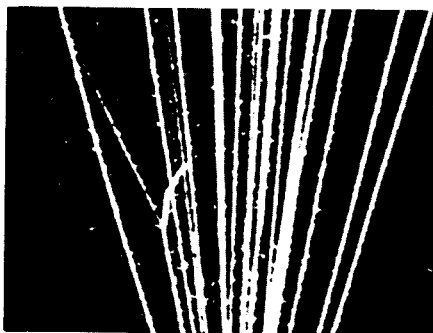


FIG. 14-4

A cloud chamber photograph of alpha tracks in nitrogen gas. The forked track was shown to be due to a speeding proton (going off to the left) and an isotope of oxygen (going off to the right). It is assumed that the alpha particle struck the nucleus of a nitrogen atom at the point where the track forks. (Photograph by P. M. S. Blackett at the Cavendish Laboratory.)

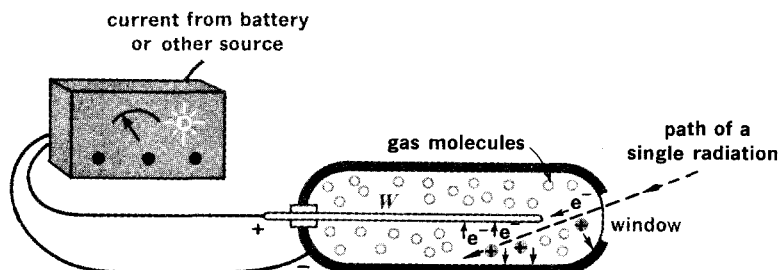


FIG. 14-5

The principle of operation of a Geiger tube.

Wilson found that, when a radioactive substance was placed in the supersaturated air of the cloud chamber, thin lines of fog or cloud emanated from the radioactive material (Fig. 14-3).

Such *cloud tracks* have been found to result whenever an ionizing radiation flies through a gas that is properly supersaturated with a condensable vapor. Evidently the flying particle or high-energy ray knocks electrons off many of the molecules in its path, forming ions that then serve as condensation centers for tiny droplets of liquid. The tracks give visible evidence of the distance traveled by different kinds of particles, the speed of travel, collisions of particles, and how the paths of the particles may be changed by outside forces, for example, electrostatic attractions or magnetic fields.

The cloud chamber has been said to provide perhaps the most obvious evidence for the existence of the atom. Not only can the tracks be observed with the unaided eye, but photographs can be made and studied at leisure (Fig. 14-4).

**Geiger Counter.** In Fig. 14-5 is shown a simplified schematic drawing of a Geiger tube. The tube operates as follows:

1. A portion of a metal tube is cut out and replaced with a "win-

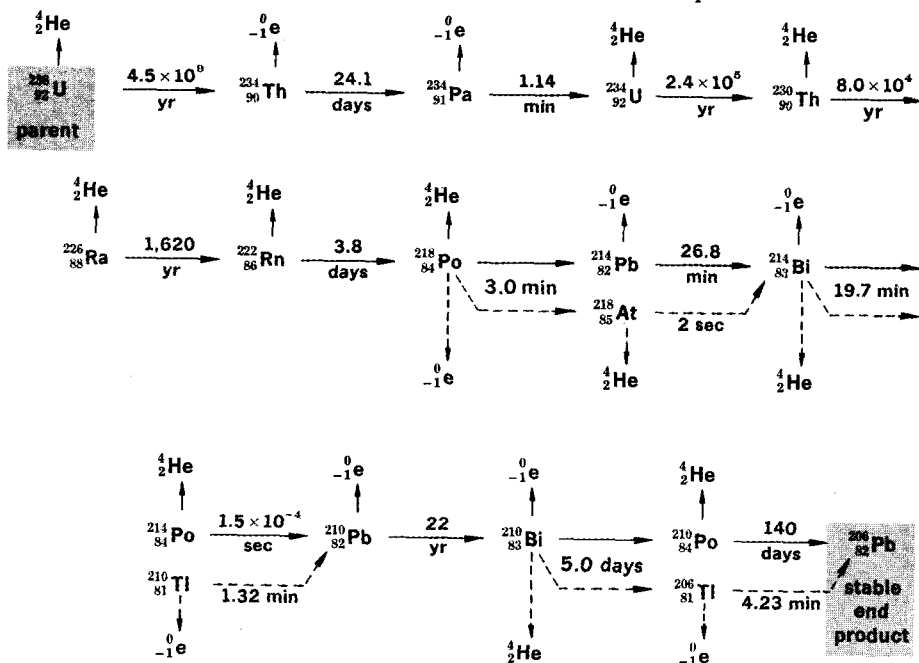
dow," a thin sheet of some material that can be penetrated by alpha or beta particles or gamma rays.<sup>1</sup>

2. A high potential is applied between an inside wire *W* and the outside of the metal tube.

3. The emitted particle or ray comes through the window and causes ionization of some of the gas molecules in the tube. The positive ions thus formed and the electrons knocked free conduct a pulse of current between the wire and the tube, and this current causes a detector light to flash or a clicker to sound. More elaborate models are provided with automatic recording devices, so that each surge of current is counted.

## NATURALLY OCCURRING RADIOACTIVE SERIES

A natural radioactive series is a collection of elements that are formed from a single radioactive element by successive emissions of alpha or beta particles. Because each emission brings about the formation of an atom of a different element, the series begins with the radioactive decay of a *parent element* and continues from atom to atom till some nonradioactive atom is formed. Uranium-238 is the parent



The  ${}^{238}\text{U}$  series of radioactive elements. Note that certain members may decay by the emission of either an  $\alpha$  or  $\beta$  particle. In cases of alternate paths or branches, the solid lines show the pathway taken by most atoms.

FIG. 14-6

<sup>1</sup> Most Geiger tubes that are used for counting alpha particles are constructed so that there is no window between the source and the sensitive volume of the tube.

## NUCLEAR REACTIONS

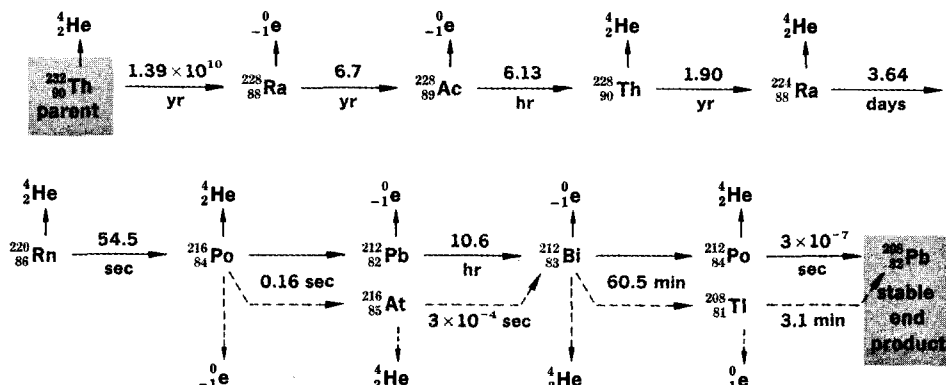


FIG. 14-7 The  $^{232}\text{Th}$  series of radioactive elements.

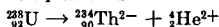
element for one naturally occurring series that contains eighteen members (see Fig. 14-6), thorium-232 is the parent of a second decay series (thirteen members, see Fig. 14-7), and uranium-235 is the parent of a third series (fifteen members). A fourth series, beginning with plutonium-241 and ending with bismuth-209 and containing fifteen members, has been unraveled recently. Because the parent of this series, plutonium-241, does not occur in the earth's minerals to a measurable extent, the series is not considered a naturally occurring one.

**Alpha Emission.** In order to understand how different elements are formed by alpha and beta emissions, let us again note that these particles are ejected from the nucleus of an atom, so that the nucleus no longer has an atomic number characteristic of the original element. For example, a uranium-238 atom that emits an alpha particle suffers a loss of two neutrons and two protons; the atomic number is thereby reduced from 92 to 90, the atomic number characteristic of atoms of thorium, and the atomic weight is decreased from 238 to 234. In other words, the uranium-238 atom becomes a thorium-234 atom by the emission of an alpha particle. The alpha particle is identical with a helium nucleus and is indicated by the symbol  $^4_2\text{He}$ . The important generalization to be noted at this point is that the emission of an alpha particle decreases the atomic number by 2 and the atomic weight by 4.

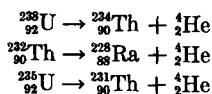
It happens that atoms of the parent members of the three principal natural radioactive series begin their decay by the emission of an alpha particle. With this information we can write the equation<sup>1</sup> for the nuclear change in the first step in the decay of each series:

<sup>1</sup> In order to focus attention on the particles of greatest interest, the nuclear chemical equations in this chapter are purposely abbreviated.

An example of a more complete equation is



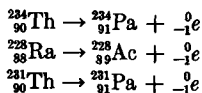
This equation takes into account the electrons around the atoms. The uranium atom



The first equation is read: "Uranium-238 decays by alpha emission to yield thorium-234."

In these equations note that the sum of the mass numbers on the left side of the arrow equals the sum of the mass numbers on the right side. Also the sum of the nuclear charges on the left side equals the sum of nuclear charges on the right side. As we shall see later, there is a slight change in mass (not mass number), although this is not indicated by the equation. The emission of an alpha particle results in a slight increase in the neutron-proton ratio, because all alpha emitters have a neutron-proton ratio greater than 1.

**Beta Emission.** The second step in each of the natural decay series involves the emission of an electron (beta particle) from the atoms formed in the first step. Because the electron comes from the nucleus, its presence is accounted for by the assumption that a neutron changes to a proton and an electron with the emission of the electron.<sup>1</sup> This process increases the number of protons by one, so the atomic number increases by one on the emission of a beta particle. However, the mass number remains unchanged; the number of protons increases by one, but the number of neutrons decreases by one also. Consequently, beta emission results in a decrease of the neutron-proton ratio. The following equations<sup>2</sup> show the second disintegration step for each of the three natural radioactive series:



The many steps leading to the formation of a stable nuclide in two of the series are shown in Figs. 14-6 and 14-7. Note that an isotope of lead is the end product of each of these natural series. The lead now present in uranium and thorium minerals was polonium, bismuth, radium, and other elements at various earlier times and, still earlier, was uranium-238, uranium-235, or thorium-232.

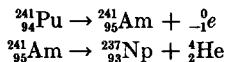
(Continued)

had 92 protons and 92 electrons. The loss of an alpha particle leaves a particle with 90 protons and 92 electrons, that is,  $\text{Th}^{2-}$ . An isolated negative ion such as this would be unstable, and the two electrons would be lost immediately, leaving the thorium atom,  ${}_{90}^{234}\text{Th}$ . As the alpha particle flies away, it bumps into molecules and atoms that slow it down; eventually it gains two electrons and becomes a helium atom,  ${}_2^4\text{He}$ .

<sup>1</sup> In beta emission, not only is an electron emitted, but also a much more elusive particle, the *antineutrino*. This particle, which has no charge and nearly zero mass, rarely interacts with matter and so can be detected only with elaborate techniques and equipment. We shall not indicate antineutrino emissions in equations.

<sup>2</sup> Note that in the equations the negative charge on the electron is indicated by the  $-1$  at the left of the  $e$ , instead of by  $e^-$ .

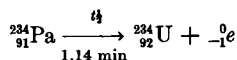
The first two steps of the plutonium-241 decay follow the opposite order of emission of the three previously described series, that is, first a beta emission and then an alpha emission:



## HALF-LIFE

How long does it take for a given sample of uranium to change to lead, or, for that matter, how long does it take for any radioactive substance to change to other substances? The time required is independent of the amount of radioactive material. For example, if it takes 1,620 years for half of a 1-g sample of radium to change to radon, the same period of time (1,620 years) is required for half of a 2-g sample to change to radon, because the 2-g sample, with twice as many radium atoms, will in all probability emit twice as many alpha particles as the 1-g sample does. The rate of radioactive change is expressed in terms of the **half-life** ( $t_{1/2}$ ) of the radioactive substance, that is, the length of time required for one-half of a given starting weight of a substance to change to other substances.

In Figs. 14-6 and 14-7 are given the half-lives of the members of two of the natural radioactive series. The half-lives are determined experimentally by counting the number of alpha and beta particles emitted in a suitable period of time by a given weight of the radioactive sample (a Geiger counter might be employed for this). It will be noted that certain radioactive elements have very short half-lives and that others have very long ones. For example, protactinium-234 is a beta emitter that emits half of its total possible beta particles in 1.14 min. Of a sample of pure  ${}^{234}\text{Pa}$  weighing 0.008 g, only 0.004 g would be left after 1.14 min, because half of the original material would have turned into  ${}^{234}\text{U}$ :



In 1.14 min more there would be only 0.002 g of  ${}^{234}\text{Pa}$ ; and after  $3 \times 1.14$ , or 3.42 min elapsed, only 0.001 g of the original 0.008 g would be left.

As indicated by Fig. 14-8, the activity of a radioactive substance theoretically never falls to zero. However, after a period of time equal to about ten half-lives, the radioactivity is so weak that it can hardly be measured. Radioactive decay is a first-order process (see Chap. 12).

We cannot predict when any certain atom will decay, but we can predict the time required for half of a large number of them to do so. Except for a few rare examples, neither the chemical state, nor the temperature, nor the pressure exerted on the radioactive element affects the frequency or the nature of its radiation. Whether the ele-

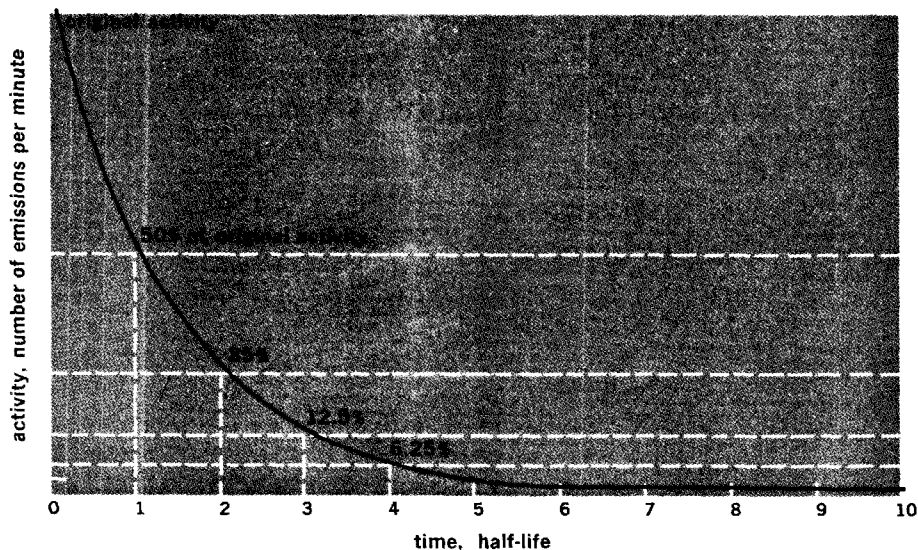


FIG. 14-8

Loss in activity of a radioactive substance with time. A plot of this type is applicable to any radioactive substance, because they all decay in accordance with the first-order rate law. Only the lengths of the half-lives differ. Compare with Fig. 12-2 for plot of another first-order reaction.

ment is present in the uncombined state or as part of a compound, its radiation and its half-life are the same.

**Curie.** A cumbersome way of specifying the amount of radiation emanating from a source is to identify the radioactive nuclides and the amounts present. The rate of emission can then be approximated from the known half-lives of the parent and daughter nuclides. For example, 238 g (1 mole) of  $^{238}\text{U}$ , with a half-life of  $4.5 \times 10^9$  years, emits  $3.01 \times 10^{23}$  ( $\frac{1}{2}$  mole) of alpha particles in one half-life. One can calculate the number of alpha particles emitted per gram in 1 min by  $^{238}\text{U}$  atoms alone from this information:

$$\begin{aligned} \text{rate} &= \frac{3.01 \times 10^{23} \text{ alpha particles}}{238 \text{ g} \times 4.5 \times 10^9 \text{ year} \times 365 \text{ days/year} \times 24 \text{ hr/day} \times 60 \text{ min/hr}} \\ &= 530,000 \text{ alpha particles from 1 g of } ^{238}\text{U} \text{ per min} \end{aligned}$$

This of course is not the total emission in 1 min, because the daughter nuclides (see Fig. 14-6) have relatively short half-lives, especially the first two. The total rate of alpha and beta emission, starting with 1 g of  $^{238}\text{U}$ , is considerably larger than the value that we have calculated.

To take into account the heterogeneous radiations from a mixture of nuclides, it has been found convenient to introduce a special unit, the curie, for specifying amounts of radioactivity. Originally, the curie was defined in terms of a certain amount of radium; today, it is

defined as a source that decays at the rate of  $3.700 \times 10^{10}$  disintegrations per second. A curie represents a rather large amount of radioactivity; one usually works in the laboratory with millicurie amounts.

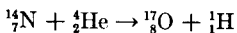
It is interesting to note some of the radioactive nuclides to which we are constantly exposed and which, to some extent, become a part of our bodies. Drinking water contains traces of compounds of uranium and uranium decay products, such as radium, in concentrations up to about  $10^{-12}$  millicurie/ml. Milk contains about  $6 \times 10^{-11}$  millicurie of  $^{40}\text{K}$  per ml, and all living matter contains a small concentration of  $^{14}\text{C}$ . It is estimated that the average human body contains enough radioactive nuclides to give rise to about 400,000 disintegrations per minute. It has been calculated that the disintegrations per minute arising from  $^{40}\text{K}$ ,  $^{14}\text{C}$ , and  $^{226}\text{Ra}$  indicate the presence in the body of about  $10^{20}$ ,  $10^{14}$ , and  $10^{11}$  atoms of  $^{40}\text{K}$ ,  $^{14}\text{C}$ , and  $^{226}\text{Ra}$ , respectively. All of these, of course, are present in the body in compounds, not as elements.

It should be pointed out here that, although the curie is a measure of the emission rate, it is not a satisfactory unit for setting up safety standards for handling radioactive materials. Because different types of emissions have different penetrating power and energies, their biological effects are not the same. Hence, from a safety point of view, the energy of the emission is extremely important.

## BOMBARDMENT REACTIONS

All the nuclear chemistry reactions that we have taken up thus far are examples of natural radioactivity; they are changes that involve only a single reactant atom and the products formed when this single atom emits a particle. As emphasized before, man can observe these radioactive changes, he can even concentrate and purify large quantities of radioactive materials, but he cannot control the nature of the particles emitted or the rate at which they are emitted.

However, there is a second class of nuclear reactions, called **bombardment reactions**, which can be controlled. These reactions result when particles of atomic or subatomic size strike atoms of matter and permanently change these atoms. The idea that an atom of one element could be purposely changed to an atom of another violated a theory that had been universally accepted since Dalton's time, but in 1919 Blackett and Rutherford reported that this indeed happened when ordinary nitrogen was exposed to the alpha particles emitted by a small sample of radium. The equation for the reaction is

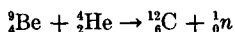


The high-speed alpha particle evidently meets a nitrogen nucleus head-on with such force that it momentarily fuses with it, making an unstable intermediate nuclear particle that then ejects a proton,  $^1_1\text{H}$ , and becomes an atom of oxygen,  $^{17}_8\text{O}$ . The proton was identified by

means of cloud chamber photographs (similar to those in Fig. 14-3) that provided the data necessary to calculate its mass and charge.

Nuclear reactions of this kind generally cannot be carried out so as to give appreciable yields, because only occasionally do the speeding alpha particles collide head-on with an atomic nucleus. This is due to the fact that the nucleus of an atom is extremely small as compared with the total size of the atom. In the case of Rutherford's work, most of the alpha particles emitted by the radium simply passed through the nitrogen gas without causing a reaction.

A most important bombardment reaction, historically speaking, was the reaction between beryllium atoms and alpha particles reported in 1930 by W. Bothe and H. Becker in Germany. This bombardment resulted in the appearance of a very penetrating radiation that had the characteristics of a stream of particles but was not deflected on passing through a magnetic field. In 1932 James Chadwick, of England, showed that the particles had masses nearly equal to that of protons but were uncharged. Thus the **neutron** was discovered:



## ACCELERATION OF CHARGED PARTICLES

It was found early in this century that, although atoms of low atomic numbers could be altered when struck by natural alpha particles, atoms of high atomic numbers were unaffected by these particles. These results were explained by assuming that the atoms with highly charged nuclei (many protons) repelled the alpha particles and prevented collisions. It was calculated, for example, that an alpha particle needs 27 million electron volts (mev) of energy in order to push in close enough to a radon nucleus so that short-range nuclear forces become effective and a radium nucleus is formed:



Alpha particles from natural sources have energies ranging from about 5 to 8 mev and are ineffective in producing reactions such as the above. Scientists the world over became concerned with the problem of increasing the speed of alpha and other subatomic particles. Soon there were invented a number of devices, called **accelerators**, that could increase the velocity of a charged particle, thereby increasing its effect on an atom struck by it. Some of the modern particle accelerators now accelerate positive ions to energies in the billion electron-volt range. Only two of these devices will be described.

**Linear Accelerator.** The **linear accelerator** consists of a number of hollow cylinders of increasing length, arranged in a straight line. An electrical system gives each alternate cylinder the same electrostatic



charge (positive or negative) and also provides for the rapid reversal of these charges. A schematic diagram of a linear accelerator is shown in Fig. 14-9. Suppose that an alpha emitter is placed at point zero. A (positive) alpha particle at 0 is attracted by cylinder 1 when 1 is negative. If the difference in potential is great enough, a particle that flies toward the middle of this cylinder tends to go right on through it. As the particle leaves the first cylinder, the charges on the odd cylinders are reversed (made positive). Because of this reversal of charge on the cylinders, the speeding particle is given a boost in speed between 1 and 2 (repelled by positive 1, attracted by negative 2). The automatic rapid reversal of charges on the odd and even cylinders causes the speed of the particles that are moving in phase with these reversals to increase steadily. Protons ( ${}^1_1\text{H}^+$ ), deuterons ( ${}^2_1\text{H}^+$ , nuclei of heavy hydrogen), alpha particles ( ${}^4_2\text{He}^{2+}$ ), and even heavy positive ions can be accelerated in this way. Linear accelerators of protons now in operation achieve energies up to 70 mev.

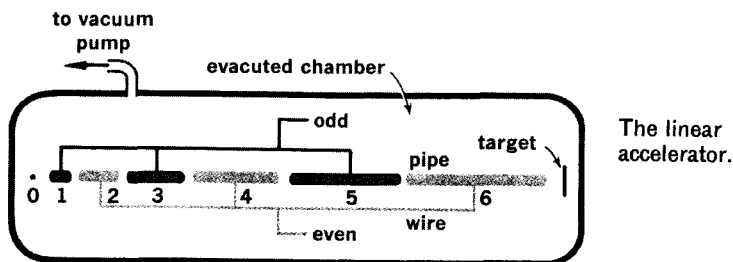
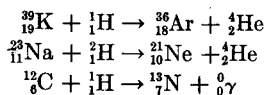


FIG. 14-9

When these high-speed projectiles strike the nuclei of the atoms in the target, nuclear chemical reactions may occur. Examples are



Note that in the third reaction only one particle is formed, and gamma radiation is emitted. Many of the nuclear changes that result in the formation of two particles also emit gamma radiation, but it is not usually included in the equation unless particular importance is attached to it.

Linear accelerators are perhaps the most efficient accelerators for electrons. Such devices now in existence in the United States and Russia accelerate electrons to 1 or 2 billion electron volts (bev), and a linear accelerator is now under construction at Stanford that will be 2 miles long when finished and is expected to accelerate electrons to energies of from 20 to 40 bev. Also the principal installation of a new National Accelerator Laboratory is a 200-bev accelerator to be built at a cost of about \$300,000,000. Cost of operating the facility is estimated at \$60,000,000/year.

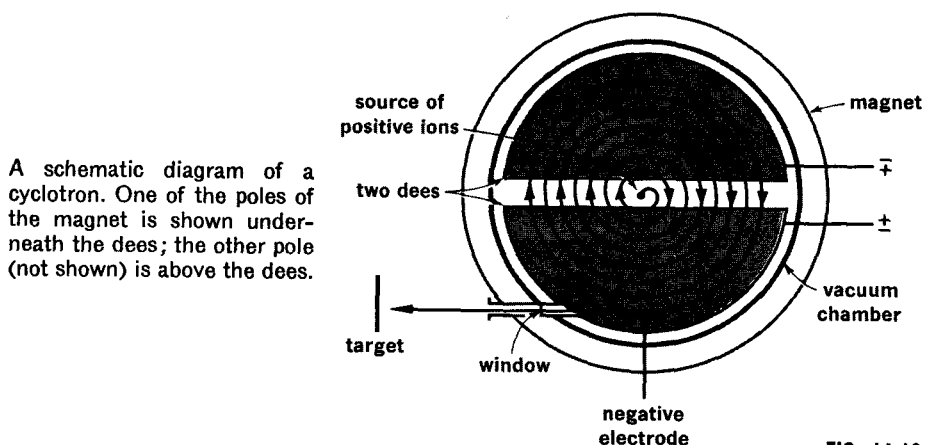


FIG. 14-10

**Cyclotron.** The cyclotron is perhaps the most useful of all the accelerators of positive particles presently employed. Its operation is based on two well-known physical laws: A charged particle is repelled by a like charge and attracted by an unlike charge, and a charged particle that is moving in a magnetic field follows a curved path.

The schematic drawing of a cyclotron in Fig. 14-10 shows six of its principal parts: (a) one of two poles of a huge electromagnet (only the bottom one is shown), (b) a hollow disk split into halves (called *dees* because of their shape), (c) a source of charged particles in the center of the apparatus, (d) a vacuum chamber that fits between the poles of the magnet and completely encloses the dees, (e) a negatively charged plate on the rim of the vacuum chamber, and (f) a "window" of thin material in the side of the vacuum chamber through which a beam of speeding particles can emerge.

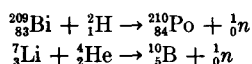
Not shown in the figure is the electrical system that controls the electrostatic charge on the dees. When one dee is positively charged, the other is negative, but these charges can be automatically and rapidly alternated.

The cyclotron operates as follows:

1. A positively charged particle produced at the source in the center is attracted toward the negatively charged dee and enters it at high speed.
2. Because of the magnetic field maintained by the huge magnets above and below the dees, the speeding positive particle is forced to move in a curved path (as shown in Fig. 14-10). While inside a dee, the particle travels in a semicircle and is soon heading back toward the gap between the dees.
3. While the positive particle is inside a dee, the charges on the dees are reversed. When the particle reaches the gap, the dee ahead of it is negative, the dee behind is positive; pulled by one dee, repelled by the other, the speeding particle is accelerated while it is in the gap.

4. Particles that are traveling in phase with the rapid reversals of the charges on the dees are accelerated each time they go from one dee to the other. As their velocity steadily increases, the radius of their spiral path increases till it is almost as large as the radius of the dees.

5. As the path of the speeding positive particles nears the rim of the vacuum chamber, the attraction of a negative electrode deflects the particles from their spiral path and causes them to fly out of the cyclotron through a window. This window is actually a thin sheet of material through which the particles can pass easily. Outside the dees, in front of the window, are placed samples of different elements to be used as *targets*. The speeding protons, deuterons, or alpha particles strike the atoms of the target element and cause nuclear chemical reactions, such as



E. O. Lawrence, the inventor of the cyclotron, reported his discovery in 1930. One of his first machines was built to fit between magnet pole pieces only 4 in. in diameter. The cyclotron has proved so useful that a number of larger ones have been built. The larger and more powerful the electromagnet, the greater the energy of the bombarding particles. One of these machines, built at the University of California and costing \$1,500,000, has magnet pole pieces 15 ft across.<sup>1</sup>

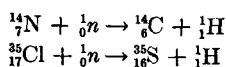
Other devices for accelerating charged particles include the betatron (electron accelerator) and the syncotron. The syncotron accelerates both positive ions and electrons (depending on construction) to energy ranges of billions of electron volts.

**Neutron Bombardments.** One of the most effective "bullets" for bringing about nuclear changes is the neutron. Unlike the positively charged protons, deuterons, and alpha particles, which are repelled by the positive nuclei of atoms, the uncharged neutrons do not require high velocities to drive them into a nucleus. Indeed, a slowly moving neutron passing close to a nucleus has a greater chance of being attracted into the nucleus than a high-speed neutron, which might race on past.

Neutrons are easily generated by bombarding light elements, such as lithium and beryllium, with alpha particles or by the reactions occurring in a nuclear reactor (discussed in Chap. 15). The neutrons

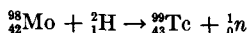
<sup>1</sup> In some cyclotrons, only one dee is used, the oscillating current being applied between it and a ground connection. As a charged particle enters or leaves the dee, it receives additional energy, so that it accelerates along a spiral path just as if two dees were used. The purpose of this arrangement is to make it possible to vary the frequency of oscillations in order to compensate for the increase in mass of the positive ion as it accelerates to very high speeds.

emitted as a result of the interaction of  ${}^7\text{Li}$  with alpha particles may cause additional reactions in materials placed in the target area. Two examples are



## SYNTHESIS OF ELEMENTS

When it was found that atoms of one element could be changed into atoms of another by nuclear bombardment, there were still blank spaces in the periodic table between elements 1 and 92. Numbers 43, 61, 85, and 87 either had not been discovered or the evidence for their discovery was open to doubt. All of these have been made since 1937 by cyclotron bombardment or by nuclear fission, and the last two have been found in minute amounts in nature. The possibility that they could exist at all was suggested by the blank spaces in the periodic table. The synthesis of these unknown elements was guided by the principle that an atom that is bombarded with a small particle may absorb all or part of the particle and become an atom with greater atomic weight and atomic number. In attempting to make the unknown element 43, it was logical to use a sample of molybdenum (number 42) as a target. The successful reaction was



The new element was named *technetium* (Greek *technetos*, artificial), because this was the first artificially made element.

## INTERCONVERSION OF MATTER AND ENERGY

In 1905, Albert Einstein formulated an equation that can be used to relate the energy change of a reaction to the difference in the masses of the reactants and products:

$$E = mc^2$$

where  $E$  is the change in energy,  $m$  is the change in mass, and  $c^2$  is the square of the velocity of light.<sup>1</sup>

When energy is expressed in ergs, mass in grams, and the speed of light in centimeters per second,

$$\begin{aligned} E \text{ (ergs)} &= m \times (3.00 \times 10^{10})^2 \\ &= m \times (9.00 \times 10^{20}) \end{aligned}$$

<sup>1</sup> It might be preferable to write this equation as  $\Delta E = \Delta m \times c^2$  to emphasize that we are dealing with the change in mass of a system that is exchanging (gaining or losing) energy with its surroundings.

If we think about just 1 g of matter being converted entirely into energy,

$$E = 1 \text{ g} \times (3.00 \times 10^{10} \text{ cm/sec})^2 \\ = 9.00 \times 10^{20} \text{ g} \times \text{cm}^2/\text{sec}^2 = 9.00 \times 10^{20} \text{ ergs}$$

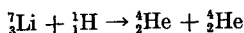
An erg is a very small unit of energy. It requires  $4.184 \times 10^7$  ergs to equal 1 calorie. Hence, when 1 g of matter is converted into energy,

$$E = 9.00 \times 10^{20} \text{ ergs} \times \frac{1 \text{ cal}}{4.184 \times 10^7 \text{ ergs}} = 2.15 \times 10^{13} \text{ cal}$$

This tremendous amount of energy, over 21 trillion calories, would be enough to heat and vaporize 9,500,000 gal of water, or equivalent to the explosion of 20,000 tons of TNT, or equivalent to one nuclear bomb of the type used in World War II.

According to Einstein's theoretical equation, when 44 tons of gasoline and 155 tons of oxygen burn and give off 400,000,000,000 cal, the loss in mass is only about 0.0185 g. Such a weight change in a total weight of 199 tons is much too small to be detected by any known instrument. It is believed that minute exchanges of mass with the surroundings do occur in every chemical reaction (whether exothermic or endothermic), but that these changes are too small to measure by weighing. In chemical reactions the law of conservation of mass holds true for all practical calculations.

However, in nuclear reactions where the energy change is much greater, the difference in the weights of reactants and products is sufficient to provide an experimental test of Einstein's theoretical equation. For example, when an atom of lithium-7 is bombarded by a proton, two alpha particles are produced:



The weights of the particles involved (as determined by means of the mass spectrograph) are:

reactants, awu		products, awu	
${}^7_3\text{Li}$	7.0160	${}^4_2\text{He}$	4.0026
${}^1_1\text{H}$	1.0078	${}^4_2\text{He}$	4.0026
	8.0238		8.0052

In this single nuclear reaction there is a loss of mass of  $8.0238 - 8.0052 = 0.0186$  awu ( $0.000000000000000000000000308$  g, or  $3.08 \times 10^{-26}$  g).

By measuring the speeds of the two alpha particles (using cloud chamber photographs), their kinetic energies can be calculated according to the equation,  $\text{KE} = \frac{1}{2}mv^2$ .

It has been experimentally determined that the total kinetic energy of the two alpha particles is equal to that calculated on the basis of  $E = mc^2$ , with  $m$  equal to  $3.08 \times 10^{-26}$  g. This agreement between

the experimental determination and the theoretical calculation based on Einstein's equation is laboratory proof that the theoretical equation is valid.

Now, if  $6.02 \times 10^{23}$  lithium atoms were involved in the nuclear reaction just described, the weight loss would be 0.0186 g. Then

$$\begin{aligned} 8.0238 \text{ g} - 8.0052 \text{ g} &= 0.0186 \text{ g} \\ E(\text{ergs}) &= 0.0186 \times (3 \times 10^{10})^2 = 1.674 \times 10^{19} \text{ ergs} \\ E(\text{cal}) &= 1.674 \times 10^{19} \text{ ergs} \times \frac{1 \text{ cal}}{4.184 \times 10^7 \text{ ergs}} \\ &= 4 \times 10^{11} \text{ cal} = 400,000,000,000 \text{ cal} \end{aligned}$$

That is, an exothermic nuclear reaction involving 7 g of lithium and 1 g of protons releases about the same amount of energy as an exothermic chemical reaction involving 44 tons of gasoline and 155 tons of oxygen.

It should be noted that the law of conservation of energy is consistent with the Einstein relation. The present view is that mass is a form of energy; conversely, any form of energy possesses inertia and can be counted as mass. In any process, the total mass-energy of an isolated system remains unchanged.

## MASS LOSS AND BINDING ENERGY

**Mass Loss.** The method of determining the masses of atomic particles by means of a mass spectrograph was described in Chap. 2. It is a fact, although a difficult one for the beginner in science to accept, that atoms always have slightly smaller masses than the sum of the masses of the particles composing them. As an example, let us calculate the mass of an atom of  ${}^4_2\text{He}$ , which contains 2 protons, 2 electrons, and 2 neutrons. In this calculation, we shall take the mass of a hydrogen atom, which contains 1 proton and 1 electron, that is 1.007825 awu, as the mass of 1 proton plus 1 electron ( ${}^{12}\text{C}$  scale). The mass<sup>1</sup> of 1 neutron on the same scale is 1.008665 awu. The calculated weight of 1  ${}^4_2\text{He}$  atom from these data is

$$\begin{aligned} 2 \times 1.007825 &= 2.015650 \text{ awu, mass of 2 protons and 2 electrons} \\ 2 \times 1.008665 &= 2.017330 \text{ awu, mass of 2 neutrons} \\ &4.032980 \text{ awu, calculated mass of } {}^4_2\text{He atom} \end{aligned}$$

Since the measured mass of a  ${}^4_2\text{He}$  atom is 4.002604, the mass loss is

$$4.032980 - 4.002604 = 0.030376 \text{ awu}$$

That is, a helium atom is about 8 per cent lighter than we would expect from the masses of the electrons, protons, and neutrons that compose it.

<sup>1</sup> The mass of a neutron cannot be measured precisely by any existing method. It is calculated from the measured masses of a proton and a deuteron and from the energy required to effect the disintegration of a deuteron into a proton and neutron.

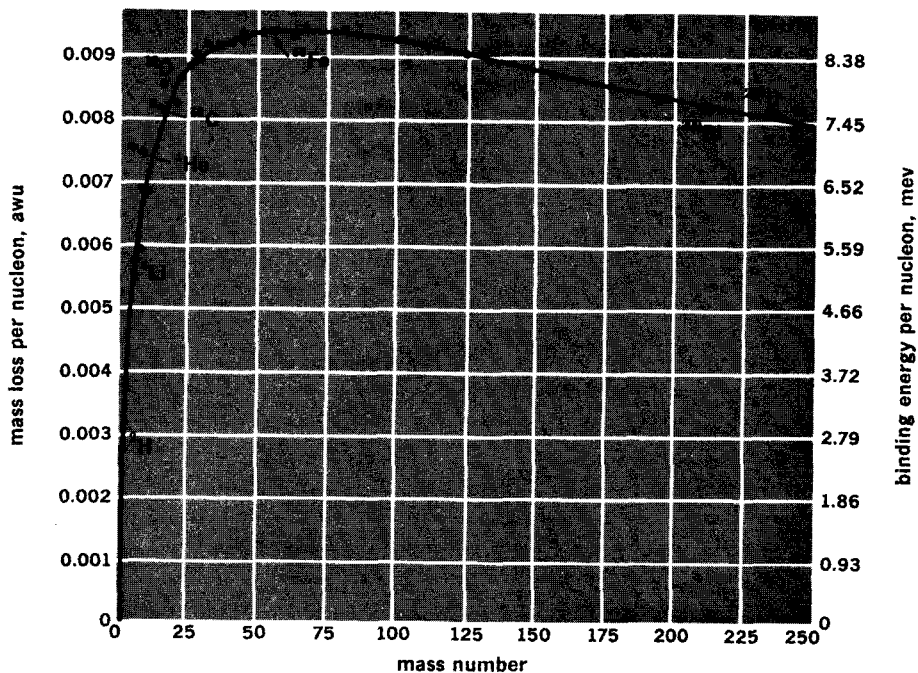


FIG. 14-11 A graph showing mass loss per nucleon (left ordinate) and binding energy per nucleon (right ordinate) versus mass number.

As a second example, let us compare the mass of one of the isotopes of iron,  $^{56}_{26}\text{Fe}$ , with its calculated mass. This atom contains 26 protons, 26 electrons, and 30 neutrons.

$$\begin{aligned} 26 \times 1.007825 &= 26.20345 \text{ awu, weight of protons and electrons} \\ 30 \times 1.008665 &= 30.25995 \text{ awu, weight of neutrons} \\ \hline &56.46340 \text{ awu, calculated weight of } ^{56}_{26}\text{Fe} \end{aligned}$$

The measured mass of  $^{56}_{26}\text{Fe}$  is 55.93493 awu. Hence, the mass loss is

$$56.46340 \text{ awu} - 55.93493 \text{ awu} = 0.52847 \text{ awu}$$

It is interesting to compare the mass losses which we have just calculated for  $^4_2\text{He}$  and  $^{56}_{26}\text{Fe}$ . We cannot simply compare 0.030376 awu with 0.52847 awu, because the former represents the mass loss of only 2 protons, 2 electrons, and 2 neutrons (6 particles), and the latter the loss for 26 protons, 26 electrons, and 30 neutrons (82 particles). We need to compare the masses of individual particles that compose the helium atom with the masses of similar particles in the iron atom. Because it is believed that the mass loss for electrons is relatively small, it is customary to allocate all the mass loss to neutrons and protons, that is, nucleons. Accordingly, the **mass loss per nucleon** is

$$\begin{aligned} \text{for } ^4_2\text{He, } 0.030376 \text{ awu} \div 4 &= 0.00759 \text{ awu per nucleon} \\ \text{for } ^{56}_{26}\text{Fe, } 0.52847 \text{ awu} \div 56 &= 0.00944 \text{ awu per nucleon} \end{aligned}$$

These calculations bring out a second interesting and important relationship. Not only do neutrons and protons have slightly smaller masses when packed in the nuclei of atoms (as compared with their masses as isolated particles), but the amount of mass loss varies from one nuclide to another. For example, the mass of a neutron or proton is smaller by 0.00759 awu when it is a part of a helium nucleus; the same particle is smaller by 0.00944 awu when it is a part of the iron nucleus.

If we make similar calculations for all the other elements, we find that the mass loss per nucleon is least for elements of very low atomic numbers, for example,  ${}^2_1\text{H}$ ,  ${}^6_3\text{Li}$ ,  ${}^7_3\text{Li}$ ,  ${}^9_4\text{Be}$ ,  ${}^{10}_4\text{Be}$ , and greatest for elements of intermediate atomic numbers, for example,  ${}^{56}_{26}\text{Fe}$ ,  ${}^{58}_{28}\text{Ni}$  (see Fig. 14-11).

**Binding Energy.** The loss of mass associated with packing neutrons, protons, and electrons together to make atoms is thought to result from the conversion of mass into energy. This energy, called the **binding energy**, may be thought of as the energy that would be necessary to break an atom into separated protons, neutrons, and electrons. The binding energy is defined as the energy equivalent of the mass loss. The energy equivalent of mass is calculated by using the relationship  $E = mc^2$ . The binding energy is usually recorded in terms of energy per nucleon, so that meaningful comparisons may be made between different nuclides. Let us calculate the binding energy per nucleon for a  ${}^4_2\text{He}$  and a  ${}^{56}_{26}\text{Fe}$  atom. We have previously calculated for these atoms the mass loss per nucleon as 0.00759 awu and 0.00944 awu, respectively. Also, we calculated on page 368 that 1 g of matter is equivalent to  $9 \times 10^{20}$  ergs of energy. Because  $1 \text{ g} = 6.02 \times 10^{23}$  awu, 1 awu of matter is equivalent to

$$\frac{9.00 \times 10^{20} \text{ ergs}}{1 \text{ g}} \times \frac{1 \text{ g}}{6.02 \times 10^{23} \text{ awu}} = 1.50 \times 10^{-3} \text{ erg/awu}$$

For the binding energy of  ${}^4_2\text{He}$ ,

$$\frac{0.00759 \text{ awu}}{\text{nucleon}} \times \frac{1.50 \times 10^{-3} \text{ erg}}{\text{awu}} = 1.14 \times 10^{-5} \text{ erg/nucleon}$$

$$\text{or} \quad \frac{1.14 \times 10^{-5} \text{ erg}}{\text{nucleon}} \times \frac{1 \text{ mev}}{1.60 \times 10^{-6} \text{ erg}} = 7.1 \text{ mev/nucleon}$$

For the mass loss of  ${}^{56}_{26}\text{Fe}$ ,

$$\frac{0.00944 \text{ awu}}{\text{nucleon}} \times \frac{1.50 \times 10^{-3} \text{ erg}}{\text{awu}} = 1.42 \times 10^{-5} \text{ erg/nucleon}$$

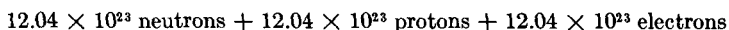
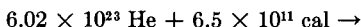
$$\text{or} \quad \frac{1.42 \times 10^{-5} \text{ erg}}{\text{nucleon}} \times \frac{1 \text{ mev}}{1.60 \times 10^{-6} \text{ erg}} = 8.9 \text{ mev/nucleon}$$



The binding energy in calories associated with a mole of helium atoms (4 g or  $6.02 \times 10^{23}$  atoms) is

$$\frac{9.00 \times 10^{20} \text{ ergs}}{1 \text{ g}} \times (4 \times 0.00759) \text{ g} \times \frac{1 \text{ cal}}{4.18 \times 10^7 \text{ ergs}} = 6.5 \times 10^{11} \text{ cal}$$

To break up a mole of helium atoms (4 g) completely into protons, neutrons, and electrons would require the addition of 650 billion cal of energy:



$$4.002604 \text{ g} + \begin{array}{c} \text{energy equivalent to} \\ \text{mass gain of} \\ 0.030376 \text{ g} \end{array} \rightarrow \text{total mass of } 4.032980 \text{ g}$$

The binding energy per nucleon for the different elements is shown graphically in Fig. 14-11. A study of this figure helps us understand several important concepts:

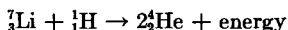
1. A number of irregularities occur for atoms of low mass numbers. In particular,  ${}^4\text{He}$ ,  ${}^{12}\text{C}$ , and  ${}^{16}\text{O}$  have relatively large mass losses and binding energies. These nuclei are especially stable for elements in this mass number range.

2. The mass losses and binding energies are greatest for nuclei with mass numbers in the vicinity of 60 (iron and nickel). Neutrons and protons have their least masses in these nuclei. The abnormally high abundance of nickel and iron in the universe is thought to be associated with the great stability of nuclei of these elements.

3. If the nucleus of a very heavy atom splits into two or more nuclei of intermediate weight (of mass 20 to 150), there would be a loss in mass, even though all protons, neutrons, and electrons were accounted for. This process can occur; it is called **nuclear fission**.

A well-known fission reaction is the splitting of a uranium-235 atom into two smaller atoms, when struck by neutrons. Fission reactions are discussed in detail in the next chapter in connection with atomic bombs and nuclear-power reactors.

4. If two or more nuclei of light atoms (mass less than 20) join to make one or more new nuclei, there could be a loss in mass, even though the resulting atoms contained all the parts of the smaller atoms. This process can occur; it is called **nuclear fusion**. An example is



Fusion reactions are also discussed in greater detail in the next chapter in connection with hydrogen bombs, stellar energy, and possible power production.

5. Because a loss of mass must result in the appearance of an equivalent amount of energy, both nuclear fission and nuclear fusion, which proceed with the loss of mass, are violently exothermic reactions.

## NUCLEAR FISSION AND THE TRANSURANIUM ELEMENTS

The decade of experimentation that led to nuclear fission, to the first elements with atomic numbers above 92 (the transuranium elements), and to nuclear bombs began shortly after the discovery of neutrons in 1932. Almost immediately scientists recognized the possible value of the neutron as a bombarding particle, because there would be no electrostatic repulsion between the highly charged nucleus and the neutral neutron. Among the first to undertake neutron bombardment were Enrico Fermi and his colleagues at the University of Rome. This group was followed shortly by Otto Hahn, Lise Meitner, and Fritz Strassmann, at the Kaiser Wilhelm Institute in Berlin, and by the Curie-Joliot group in Paris.

One aim of this early work (1934 to 1938) was to prepare elements beyond uranium, the last element in the periodic classification at that time. Fermi and his associates predicted that  $^{238}\text{U}$ , on neutron capture, should form unstable  $^{239}\text{U}$ , which by beta decay should form an element with atomic number 93, and that element 93 should by beta decay form element 94.

In the early stages of this work it was found that neutron bombardment of uranium did indeed produce new radioactive nuclides, as evidenced by the new kind of activities and half-lives of the resulting products. However, the identity of the products was extremely difficult to establish, because the experimental work involved fantastically small amounts of material, so that chemical separation of the products by conventional methods was impossible. Also, the firm belief among physicists and chemists that nuclei could not be split undoubtedly contributed to the delay in identifying the new nuclides.

Late in 1938, Hahn and Strassmann identified barium as a product of the neutron bombardment of uranium; only the splitting of the uranium atoms could account for this amazing finding. The discovery of the Hahn-Strassmann group was passed on by letter to Lise Meitner, who had fled from Nazi Germany to work in Sweden and Denmark. She and Otto Frisch, her cousin, put forward a theoretical explanation of the process and coined the term "fission" to describe the splitting of uranium atoms in such reactions that we write today as



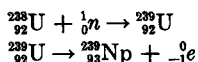
If such a fission reaction takes place, there should be a large amount of energy released, because the binding energies of the fission products are greater than for uranium (see Fig. 14-11). Working in Neils Bohr's laboratory in Copenhagen, Frisch, on January 15, 1939, found experimentally that great energies were released when uranium was bombarded with neutrons. This result showed that fission reactions were indeed occurring.

In January, 1939, Bohr, while visiting the United States, passed on the information about the uranium fission and the high-energy

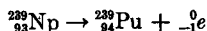
emission to physicists in this country. The conclusions were quickly verified in this country by Fermi, who had fled Italy and was then at Columbia University, and by J. R. Dunning, F. G. Slack, and E. T. Booth at Columbia University, and E. M. McMillan at the University of California at Berkeley.

The foreign-born scientists working in this country were gravely concerned with the military potential of uranium fission and with the possibility that this potential might be developed and used by the Germans. In a letter to President Franklin D. Roosevelt dated August 2, 1939, Albert Einstein called attention to these possibilities. Thus began a chain of events that led the United States into a vast amount of research in the field of nuclear chemistry and physics. Results directly connected with the war effort included the large-scale separation of the  $^{235}\text{U}$  isotope from natural uranium, the synthetic production of  $^{239}\text{Pu}$ , and the production of two fission bombs that were dropped on cities in Japan in 1945.

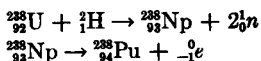
In the meantime, work on the elements beyond uranium was not forgotten. In 1940, McMillan and P. H. Abelson at Berkeley found that, when a thin foil of uranium was bombarded with neutrons, the recoil energies of the atoms formed by fission of  $^{235}\text{U}$  carried them out of the foil. Thus, they were not plagued with the radioactive fission products as previous investigators had been. They were then able to show that element 93 was formed from  $^{238}\text{U}$ , as predicted by Fermi some six years earlier:



The name *neptunium* was given to element 93, because the planet Neptune is beyond Uranus, just as the new element was beyond uranium in the periodic classification. Because of the very small amount of neptunium produced in these experiments, McMillan was unable to show that element 94 was formed by the beta decay of neptunium. This is now known to take place:



The study of the transuranium elements at Berkeley was continued by G. T. Seaborg and his associates. To provide for larger-scale experiments, they bombarded uranium with cyclotron-accelerated deuterium and were able to obtain enough neptunium to study it more fully and to show that it decays to form element 94:



The new element was named *plutonium* after the planet Pluto, which is just beyond Neptune.

Seaborg and his group at the University of California at Berkeley have played the major role in the development of transuranium-

elements chemistry. In addition to neptunium and plutonium, the Berkeley group is credited with the discovery of americium, curium, berkelium, californium, mendelevium, and lawrencium. Element 102 has also been made at Berkeley, but credit for the first synthesis has been a matter of dispute with a group that worked under the auspices of the Nobel Institute. If it is decided that the latter group reported the discovery prematurely, the name nobelium for 102 may be changed.

Late in the summer of 1964, the Soviet news agency reported that element 104 had been made by U.S.S.R. scientists by bombarding plutonium-242 with high speed neon-22 ions. Its half-life was reported as 0.3 sec. Study of the newest element was made on a total of 170 atoms.

The reaction that led to the initial discovery of each transuranium element now known is shown in Table 14-2.

*Reactions by which transuranium elements were first observed*

TABLE 14-2

atomic number	symbol	name	reaction
93	Np	neptunium	$^{238}_{92}\text{U} + {}^1_0\text{n} \rightarrow {}^{239}_{93}\text{Np} + {}^0_{-1}\text{e}$
94	Pu	plutonium	$^{238}_{92}\text{U} + {}^2_1\text{H} \rightarrow {}^{238}_{93}\text{Np} + 2{}^1_0\text{n}$ $^{238}_{93}\text{Np} \rightarrow {}^{238}_{94}\text{Pu} + {}^0_{-1}\text{e}$
95	Am	americium	$^{239}_{94}\text{Pu} + {}^1_0\text{n} \rightarrow {}^{240}_{95}\text{Am} + {}^0_{-1}\text{e}$
96	Cm	curium	$^{239}_{94}\text{Pu} + {}^4_2\text{He} \rightarrow {}^{242}_{96}\text{Cm} + {}^1_0\text{n}$
97	Bk	berkelium	$^{241}_{95}\text{Am} + {}^4_2\text{He} \rightarrow {}^{243}_{97}\text{Bk} + 2{}^1_0\text{n}$
98	Cf	californium	$^{242}_{96}\text{Cm} + {}^4_2\text{He} \rightarrow {}^{246}_{98}\text{Cf} + {}^1_0\text{n}$
99	Es	einsteinium	$^{238}_{92}\text{U} + 15{}^1_0\text{n} \rightarrow {}^{253}_{99}\text{Es} + 7{}^0_{-1}\text{e}^\dagger$
100	Fm	fermium	$^{238}_{92}\text{U} + 17{}^1_0\text{n} \rightarrow {}^{255}_{100}\text{Fm} + 8{}^0_{-1}\text{e}^\dagger$
101	Mv	mendelevium	$^{253}_{99}\text{Es} + {}^4_2\text{He} \rightarrow {}^{256}_{101}\text{Mv} + {}^1_0\text{n}$
102	No*	nobelium	$^{246}_{96}\text{Cm} + {}^{12}_6\text{C} \rightarrow {}^{254}_{102}\text{No} + 4{}^1_0\text{n}$
103	Lr	lawrencium	$^{252}_{98}\text{Cf} + {}^{10}_5\text{B} \rightarrow {}^{257}_{103}\text{Lr} + 5{}^1_0\text{n}$
104	?	?	$^{242}_{94}\text{Pu} + {}^{22}_{10}\text{Ne} \rightarrow {}^{260}_{104}^? + 4{}^1_0\text{n}^\ddagger$

\*Name not officially accepted.

†Overall reaction to account for new element on the basis of intense neutron bombardment.

‡Reported by U.S.S.R. scientists in 1964.

## CHAPTER REVIEW

### Terms

Transmutation, radioactivity, isotopes, nuclides, radioactive decay, neutron-proton ratio, magic numbers, nucleon; alpha, beta, and gamma emissions; ionizing radiations, fluorescence, cloud chamber, Geiger counter, radio-

active series, half-life, curie, bombardment reactions, linear accelerator, cyclotron,  $E = mc^2$ , mass loss, binding energy, nuclear fission, nuclear fusion, transuranium elements.

### Exercises

1. *a.* Give the symbols for four possible nuclides with mass numbers near 210 such that none are related as isotopes.  
*b.* Give the symbols for four possible nuclides with mass numbers near 210 such that all are related as isotopes.
2. How does the neutron-proton ratio for stable nuclides of mass numbers near 20 differ from the ratio for mass numbers near 200?
3. How do radioactive changes differ from ordinary chemical changes with respect to what happens to the atoms?
4. *a.* In the series described in Fig. 14-7, consider the two nuclides that decay to yield the stable end product. Calculate the neutron-proton ratios of  $^{208}\text{Tl}$ ,  $^{212}\text{Po}$ , and  $^{208}\text{Pb}$ .  
*b.* Consider the hypothetical cases of alpha emission by  $^{208}\text{Tl}$  and beta emission by  $^{212}\text{Po}$ ; compare the neutron-proton ratios for the hypothetical products with the ratio for the stable  $^{208}\text{Pb}$ .
5. Helium gas is often occluded in rocks and minerals that contain radioactive substances. Account for its presence.
6. *a.* If the neutron-proton ratio for maximum stability is about 1.52 in the mass number range from 206 to 212, will the unstable nuclide  $^{211}\text{Bi}$  yield a nuclide nearer the stable ratio by emitting an alpha or a beta particle?  
*b.* Repeat (*a*) for the unstable nuclide  $^{211}\text{Po}$ .
7. Which is more likely to have the greater number of stable isotopes, indium (In), tin (Sn), or antimony (Sb)?
8. A sample of a beta emitter is placed in a discharge tube of the type shown in Fig. 2-7; then the tube is highly evacuated and sealed. In an identical tube an alpha emitter is similarly sealed. Immediately after sealing, an electric discharge is passed through each tube; the discharges appear to be the same as for any ordinary discharge tubes. After standing for a month, the tubes are tested again. This time, one of the tubes shows a quite different type of discharge, whereas the other shows no change at all. Explain fully.
9. By means of a clearly labeled diagram, explain the operation of a cloud chamber.
10. *a.* Show that alpha emission for all probable cases results in an increase in the neutron-proton ratio, but that, for the hypothetical case of an initial ratio less than unity, an alpha emission would result in a decrease.  
*b.* Show that beta emission always leads to a decrease in the neutron-proton ratio.

11. Why must a battery or some other source of electricity be used to make a Geiger counter operate?
12.
  - a. A radioactive series, some of whose members exist only in minute traces in nature, includes  $^{241}\text{Pu}$  as the probable parent and  $^{209}\text{Bi}$  as the stable end product. How many alpha and beta emissions are involved in the change of a plutonium nuclide into bismuth?
  - b. How would the answer to (a) be affected if there were four branches (alternate decay paths) in the decay scheme?
  - c. How many members would the series have if there were no branches? Four branches?
  - d. If 15 members of the series have been discovered, how many branches has the series?
13.
  - a. What must be the end product of the natural radioactive series that begins with  $^{235}\text{U}$  and involves seven alpha and four beta emissions?
  - b. If the  $^{235}\text{U}$  series has 15 members, how many branches must it have?
14. An atom of  $^{239}\text{U}$  of course has the electronic configuration characteristic of uranium atoms. What happens to the configuration when a uranium nucleus emits an alpha particle and changes into a thorium nucleus?
15. Make a plot of atomic number versus mass number for the members of one of the natural radioactive series.
16. Starting with a 2-g sample of  $^{234}\text{Th}$ , how much remains at the end of 48 days? The half-life of  $^{234}\text{Th}$  is 24 days.
17. A Geiger counter showed that a radioactive substance gave a reading of 5,180 counts per minute in January, 1951; by January, 1966, the reading had fallen to 81 counts per minute. What is the half-life of the substance?
18.
  - a. B. B. Boltwood and E. Rutherford reported in the *Philosophical Magazine*, **22**: 586 (1911), that the radioactive decay per gram of impure radium produced  $3.4 \times 10^{10}$  alphas/sec and that this alpha radiation gave rise to helium gas that collected at the rate of 0.039 ml/year (measured at STP). From these data, calculate a value for Avogadro's number (that is, the number of helium atoms per mole of helium).
  - b. Suppose the radium contained traces of short-lived alpha-emitting daughter elements. How would this affect the validity of your calculation in (a)?
19.
  - a. Using the data in Exercise 18 and the formula in Exercise 10 of Chap. 12, calculate the half-life of radium and compare your answer with that given in the text for  $^{226}\text{Ra}$ . (Suggestion: Calculate  $k$  by dividing the number of radium atoms decaying per second by the total number of radium atoms initially present in the sample. This approximate calculation is only valid for nuclides of long half-life.)
  - b. Suppose the radium contained traces of short-lived alpha-emitting daughter elements. How would this affect the validity of your calculation in (a)?
20. How many curies of radiation are there per gram of impure radium, according to the data in Exercise 18; millicuries per milligram? Would it be

- possible for some nuclide (not necessarily of radium) to have an activity of 1 curie/mg?
21. State in your own words the physical laws on which the operation of the cyclotron is based. Repeat for the linear accelerator.
  22. Calculate the volume of milk in gallons that would contain 1 curie of radioactive potassium,  $^{40}\text{K}$ .
  23. A millicurie of one radioactive isotope might be safely handled in a sealed glass tube, whereas a millicurie of another isotope might be too dangerous to be so handled. Explain.
  24. Even though alpha particles have very little penetrating power, they can be extremely dangerous if taken into the body. Explain.
  25. Using a clearly labeled diagram, explain why naturally emitted alpha particles might be able to transmute carbon atoms into nitrogen atoms but not lead atoms into bismuth atoms.
  26. What physical principles are common to the linear accelerator and to the cyclotron? What principles are important to one but not the other? Can either apparatus accelerate neutrons?
  27. Balance the following nuclear equations by filling in data for the question marks; some are equations for natural radioactivity, but most are not:
 

a. $^{35}_{17}\text{Cl} + {}^1_0n \rightarrow {}^{34}_{16}\text{S} + ?$	h. $? + {}^1_1\text{H} \rightarrow {}^{28}_{14}\text{Si} + \gamma$
b. $^{96}_{42}\text{Mo} + {}^4_2\text{He} \rightarrow {}^{100}_{43}\text{Tc} + ?$	i. $^{238}_{92}\text{U} + {}^4_2\text{He} \rightarrow ? + {}^1_0n$
c. $^{56}_{26}\text{Fe} + {}^3_1\text{H} \rightarrow ? + 2{}^1_0n$	j. $^{40}_{19}\text{K} \rightarrow {}^0_{-1}e + ?$
d. $^{63}_{29}\text{Cu} + ? \rightarrow {}^{65}_{30}\text{Zn}$	k. ${}^6_3\text{Li} + {}^1_1\text{H} \rightarrow {}^4_2\text{He} + ?$
e. $^{227}_{89}\text{Ac} \rightarrow {}^4_2\text{He} + ?$	l. $? \rightarrow {}^4_2\text{He} + {}^{230}_{90}\text{Th}$
f. $^{210}_{82}\text{Pb} \rightarrow {}^0_{-1}e + ?$	m. $^{12}_6\text{C} + ? \rightarrow {}^{13}_7\text{N} + {}^0_0\gamma$
g. $^{23}_{11}\text{Na} + ? \rightarrow {}^{23}_{12}\text{Mg} + {}^1_0n$	n. $^{224}_{88}\text{Ra} \rightarrow ? + {}^{220}_{86}\text{Rn}$
  28. Max von Laue has pointed out (in *Albert Einstein: Philosopher—Scientist*, Harper Torchbooks, 1959, p. 530) that Hans Landolt, in his classical conservation of mass studies from 1893 to 1909, found that for a reaction such as  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ ,  $\Delta H = -136.6$  kcal, the masses of the products and reactants were constant within his limit of accuracy, 1 part in 1 million. Calculate the change in mass for the formation of water in parts per million on the basis of Einstein's equation. What fraction of Landolt's limit of accuracy is the mass loss?
  29. What property of the neutron makes it a more effective bombarding particle than particles like  $\text{H}^+$ ,  ${}^3\text{H}^+$ ,  ${}^4\text{He}^{2+}$ ?
  30. Only high-energy protons and helium nuclei, not low-energy ones, are effective in bringing about nuclear reactions. On the other hand, low-energy neutrons may be more effective than fast neutrons. Account for this difference.
  31. The study of alpha bombardment led to the discovery of transmutation of elements, but no such changes have been observed as the result of beta bombardment. What is a plausible explanation of this? Is there a factor that might be expected to make beta particles effective in bombarding nuclei?

32. By examination of Fig. 14-11, pick out two or three nuclei that are remarkably more stable than others of about the same mass number. Show if any of those which you chose have magic numbers of protons or neutrons, or both.
33. Based on data read from Fig. 14-11, calculate the average energy evolved in ergs per nucleon for the reaction  $^2\text{H} + ^6\text{Li} \rightarrow 2^4\text{He}$ . Also, calculate the energy in calories per gram of helium produced and in kilocalories per mole.
34. Would the splitting of a  $^{56}_{26}\text{Fe}$  nucleus into two  $^{27}_{13}\text{Al}$  nuclei be an exo- or endothermic process?
35. Calculate the mass loss in an atom of  $^{16}\text{O}$  (the isotopic weight is 15.99491 awu). On the basis of your calculation here and the similar calculation for helium in the text, would the fusion of four helium nuclei to form an oxygen atom ( $4^4\text{He} \rightarrow ^{16}\text{O}$ ) be an endothermic or an exothermic process?
36. Calculate the amount of heat liberated or absorbed when 4 moles of helium is converted into oxygen (see Exercise 35).
37.
  - a. The mass of a  $^{35}_{17}\text{Cl}$  atom is 34.96885 awu. Calculate the mass loss for this atom and its mass loss per nucleon.
  - b. Calculate the binding energy per nucleon for the  $^{35}_{17}\text{Cl}$  atom.
  - c. How many moles of  $^4_2\text{He}$  would have to be synthesized from protons, neutrons, and electrons to yield sufficient energy to convert a mole of  $^{35}_{17}\text{Cl}$  into free protons, neutrons, and electrons?
38. Using Fig. 14-11, give hypothetical equations, but using specific nuclides as examples, of the following:
  - a. A fission reaction that would be exothermic.
  - b. A fission reaction that would be endothermic.
  - c. A fusion reaction that would be exothermic.
  - d. A fusion reaction that would be endothermic.
  - e. Which of the foregoing could obviously not be used to produce an explosion?
39. Professor Seaborg has suggested that the limit to the production of new elements by present techniques may lie at about atomic number 108. What are some factors that obviously seem to limit the number of elements that can be synthesized?

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# APPLICATIONS OF NUCLEAR REACTIONS



Spurred on by the desire to build superbombs and other instruments of war, man in the past two decades has achieved unprecedented success in taking advantage of forty-five years of fundamental research on radioactivity in developing tools for waging war. He has also developed methods of producing useful power and of investigating the nature of intricate chemical and biological changes. It is to be hoped that we are now entering an era in which peacetime applications will completely overshadow destructive applications. It is our objective here to discuss examples of both these applications in order to give the student a fundamental understanding of this field.

## APPLICATIONS OF THE FISSION PROCESS

*Fission Bombs.* The nuclear bombs developed toward the close of World War II were of the fission type. Uranium-235 constituted the fissionable material in the first bomb used in warfare, and plutonium-239 was the fissionable material in the second one.

Of interest is the fact that, although all the elements heavier than bismuth are radioactive, only the nucleus of one natural nuclide, uranium-235, splits almost instantaneously into two fragments (undergoes fission) when struck by a thermal neutron.<sup>1</sup> Among the synthetic isotopes, plutonium-239 and uranium-233 have the same property. Their production is discussed later in this chapter.

<sup>1</sup> Neutrons that have kinetic energies comparable with the kinetic energies of gas molecules at ordinary temperatures are referred to variously as slow-moving neutrons, low-energy neutrons, or thermal neutrons.

# APPLICATIONS OF NUCLEAR REACTIONS

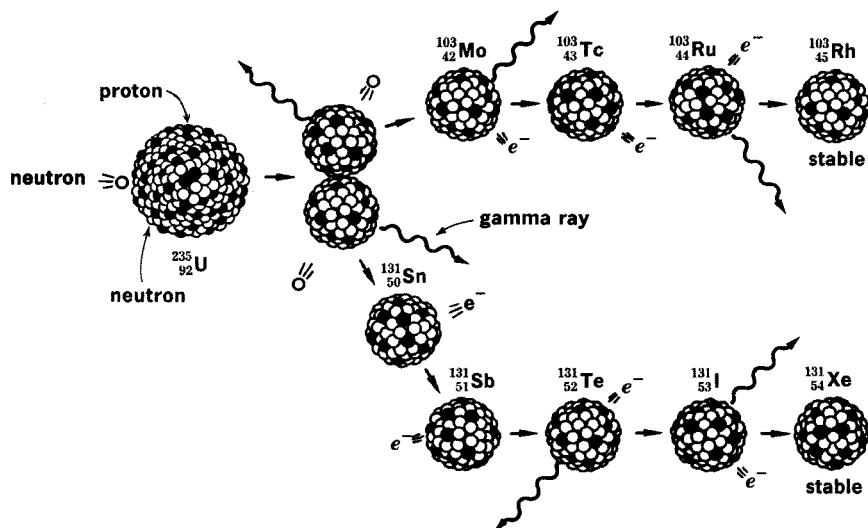
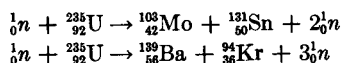


FIG. 15-1

A uranium-235 nucleus after capturing a neutron (left) splits into two smaller nuclei with the emission of gamma rays and two or three neutrons. The uranium-235 nuclei can split in over 30 ways, producing a total of about 200 radioactive species, generally with atomic numbers 30 to 64 and masses 72 to 161.

The fissioning process for uranium-235 nuclei is represented schematically in Fig. 15-1. The equations below represent two of the 30 or more ways that uranium atoms may split; of great importance is the fact that each fission produces more neutrons:



The fission products,  ${}^{103}_{42}\text{Mo}$ ,  ${}^{131}_{50}\text{Sn}$ ,  ${}^{139}_{56}\text{Ba}$ , and  ${}^{94}_{36}\text{Kr}$ , emit beta and gamma rays till stable isotopes are formed.

**CRITICAL MASS.** With the discovery that two or three neutrons are released when a uranium-235 atom fissions, it was realized that, under the proper conditions, neutrons could multiply rapidly, so that billions would become available, and the fission process would then proceed on a huge scale with the release of a tremendous amount of energy. To see what these conditions are, we begin by considering natural uranium.

In nature, only a low concentration of uranium-235 is dispersed in uranium-238, so that there is small probability of a neutron hitting a  ${}^{235}\text{U}$  atom. Some fissions occur because of neutrons that are set in motion by cosmic radiation, but natural fissions are relatively rare and are so widely separated that the energy is easily dissipated and the extra neutrons are absorbed by the nonfissionable atoms in the mineral.

Next, we consider a sphere of pure uranium-235. When the sphere is small, about the size of a marble, most of the neutrons that are produced by occasional fissioning of uranium-235 atoms induced by cosmic rays escape from the sphere. This is so because the nucleus of the atom is extremely small compared with the total volume of the atom. It is quite improbable, therefore, that a neutron will accidentally hit a tiny nucleus as it passes through the atoms in a thin piece of uranium. Under these conditions, the chain reaction is not self-sustaining.

Now we shall consider a larger sphere of pure uranium-235. Because the neutrons have to travel through a larger number of atoms before leaving this sphere, more of them will collide with uranium-235 nuclei than in a smaller sphere.

As the sphere increases in size (perhaps to a little larger than a baseball in the case of uranium-235), a mass will be reached in which, on the average, one and only one neutron from each nucleus that is undergoing fission produces splitting in another nucleus. The remaining neutrons escape or are lost.<sup>1</sup> The chain reaction is now self-sustaining.

The amount and arrangement of fissionable material in which each fission produces only one new fission is called the **critical mass**; the neutron reproduction factor equals 1. Masses below this are said to be **subcritical**; the neutron reproduction factor is less than 1. Masses larger than the critical mass are said to be **supercritical**; the neutron reproduction factor is greater than 1 (see Fig. 15-2).

A schematic representation of how neutrons become very numerous in a supercritical mass of  $^{235}\text{U}$ . (Only nuclei are represented; because a nucleus comprises only about 1/10,000th of the atom, its size is necessarily exaggerated here relative to the space between it and other nuclei.)

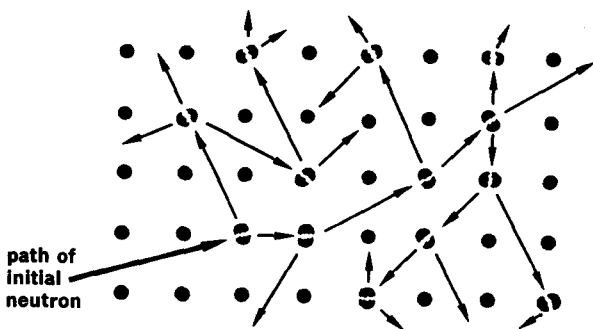


FIG. 15-2

In supercritical masses of fissionable substances, the reproduction of neutrons takes place at a fantastic rate, so that the supercritical mass is virtually a beehive of neutrons within one-millionth of a second. Under these conditions, fissioning is so rapid that the temperature rises to about  $10,000,000^{\circ}\text{C}$  or more. Within a fraction of a second

<sup>1</sup> The loss of neutrons may be due to a variety of factors in addition to the obvious one of missing all surrounding nuclei and speeding off into space. Bumping into the nuclei of impurities uses up some neutrons, and ineffective collisions with  $^{238}\text{U}$  nuclei uses up a considerable number. Approximately five-sixths of the collisions with  $^{235}\text{U}$  produce fission; one-sixth produce  $^{236}\text{U}$  nuclei.

## APPLICATIONS OF NUCLEAR REACTIONS

after becoming supercritical, the whole mass explodes into many subcritical masses.

To cause an atomic bomb to explode, sufficient subcritical masses are suddenly brought together to make a supercritical mass. The neutrons and fissioning atoms must be held together long enough for the chain reaction to build up to a considerable rate. This is done by enclosing the uranium (or plutonium) in a strong, dense case that reflects neutrons back into the fissionable material and also retards the bomb burst (Fig. 15-3).

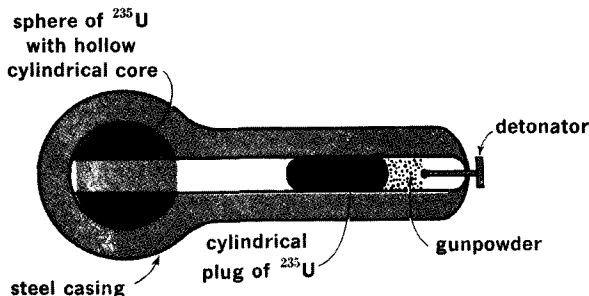


FIG. 15-3

A possible method for exploding a fission bomb. Two subcritical masses—a hollow sphere of uranium-235 and a cylinder of uranium-235 machined so as to fit the hollow sphere—are located at opposite ends of a steel casing. When the gunpowder is exploded, the uranium-235 cylinder is forced through the open bore of the steel casing into the hollow uranium-235 sphere to form a supercritical mass of uranium-235.

The explosive power of fission and fusion bombs is usually described in terms of megatons. One **megaton** is equivalent to the energy released by the explosion of 1 million tons of common explosives, such as TNT. The fissioning of 110 lb of  $^{235}\text{U}$  or  $^{238}\text{Pu}$  releases this much energy. However, bombs that depend on fission alone contain only a few pounds of fissionable material, because the chain reaction rapidly builds up into an explosion, so that unreacted  $^{235}\text{U}$  or  $^{238}\text{Pu}$  is simply scattered in noncritical masses. The fission bombs dropped on Japan were about 0.02-megaton bombs.

**FALL-OUT.** After an explosion, the highly compressed gases (even uranium and the metal casing are vaporized at  $10,000,000^\circ\text{C}$ ) expand very rapidly over an area of 100 miles or so. Although a proportion of the bomb "ashes" may fall to the earth fairly close to the explosion site, much is carried by air currents to all parts of the globe. Gradually, rain and snow carry this fall-out to the earth, where it constitutes a hazard, because of the radioactive material present.

To understand why so much radioactive material is present in the bomb ashes, we again consider the two equations given earlier for typical fission reactions. The atoms produced were  $^{103}_{42}\text{Mo}$ ,  $^{131}_{50}\text{Sn}$ ,  $^{139}_{56}\text{Ba}$ , and  $^{94}_{36}\text{Kr}$ . When we compare the neutron-proton ratio of these atoms

with those for the common nuclides of these elements, we see that they lie outside the band of stable nuclei (see Fig. 14-1). The unstable initial fission products emit beta particles (and gamma rays) till a nuclide with a stable neutron-proton ratio is produced (see Fig. 15-1).

Because the half-lives of many of the unstable nuclides that result from fissioning range from months to several years, some of the radioactivity of the large number of bombs already exploded in the atmosphere will be with us for many years to come. All but two of these bombs have been exploded in bomb-testing programs in the United States, Russia, and other nations. Testing in the atmosphere has been discontinued by most of the major powers because of the fall-out danger.

Certain unstable nuclides from the bomb ashes—strontium-90 and cesium-137, for example—are picked up by growing plants and later by man from such foods as cereals, milk, and tea. Strontium-90, like calcium, accumulates in bones, especially in those of children, where it is said to cause bone cancer and leukemia.

*Source of Fissionable Material.* Of the uranium present in a uranium ore, only 0.7 per cent is the 235-isotope; the remainder is essentially uranium-238. Separation of the isotopes of an element is very difficult, because the isotopes have practically identical chemical properties, a fact that prevents the use of ordinary methods of separation.

**GASEOUS DIFFUSION SEPARATION.** The rates of diffusion of gases depend on their molecular weights, in accordance with the following expression:

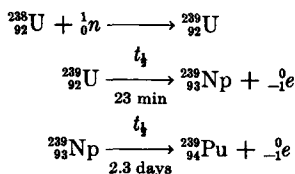
$$\frac{r_1}{r_2} = \frac{\sqrt{m_2}}{\sqrt{m_1}}$$

where  $m_1$  and  $m_2$  are the molecular weights of two different molecules, and  $r_1$  and  $r_2$  are the rates of diffusion (Graham's law; see Chap. 8). Above 56°C, uranium hexafluoride,  $\text{UF}_6$ , is a gas whose molecules consist of  $^{235}\text{UF}_6$  and  $^{238}\text{UF}_6$ . The weights of these molecules are 349 and 352 awu, respectively. Hence, if a portion of a sample of uranium hexafluoride diffuses through a porous barrier into a vacuum, the portion that diffuses will contain a slightly higher percentage of  $^{235}\text{UF}_6$  than the undiffused portion does. If a part of the enriched portion is allowed to diffuse through a second barrier, further enrichment occurs. If the process is repeated a sufficient number of times, pure  $^{235}\text{UF}_6$  is obtained. As carried out at Oak Ridge, Tennessee, the portion of the gas that remains behind a particular barrier is recirculated to a previous stage. Several thousand diffusions are necessary to bring about separation of the two isotopes.

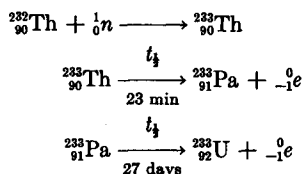
**PLUTONIUM-239 AND URANIUM-233.** The scarcity of uranium-235 in nature stimulated development of a way of synthesizing fissionable material. This has been accomplished by converting nonfissionable

uranium-238 into fissionable plutonium-239 and converting thorium-232 into uranium-233 by neutron capture in nuclear reactors. The equations are as follows:

For plutonium-239 production:



For uranium-233 production:



The second atomic bomb dropped in World War II contained plutonium as the fissionable material. The plutonium was produced in a huge nuclear reactor at Hanford, Washington, in accordance with the reactions in the equations above. It is also being produced in plants located on the Savannah River in South Carolina.

**Nuclear Reactor.** The fission of uranium-235, uranium-233, and plutonium-239 can be controlled so that the chain reaction occurs without a disastrous explosion. Under these conditions of control, the heat that is liberated in a fraction of a second by an atomic explosion is liberated over a period of several days or weeks. One apparatus that makes this possible is the atomic pile, or **nuclear reactor**. Several dozen of these reactors have now been built in the United States and abroad. Although they may differ from one another in design, type of fuel, coolant, etc., all operate on the same fundamental principles. We can make these principles clear by discussing the X-10 reactor, the first reactor of significant power level to be built.<sup>1</sup> Constructed in 1943 at Oak Ridge, Tennessee, the X-10 served as a pilot plant for the large plutonium-producing reactors put into operation at Hanford, Washington, in September of 1944. Figure 15-4 is a schematic drawing of the X-10 reactor. The following points serve to accent the principles involved:

1. The reactor is essentially a huge cube made of bricks of graphite, surrounded by a shield of concrete 7 ft thick. The graphite is called

<sup>1</sup> The first reactor was constructed at the University of Chicago by Fermi and his colleagues. Built of graphite blocks and slightly more than one-half ton of natural uranium, it was used to demonstrate, in December of 1942, that the uranium-fissioning chain reaction can be sustained at a controlled rate.

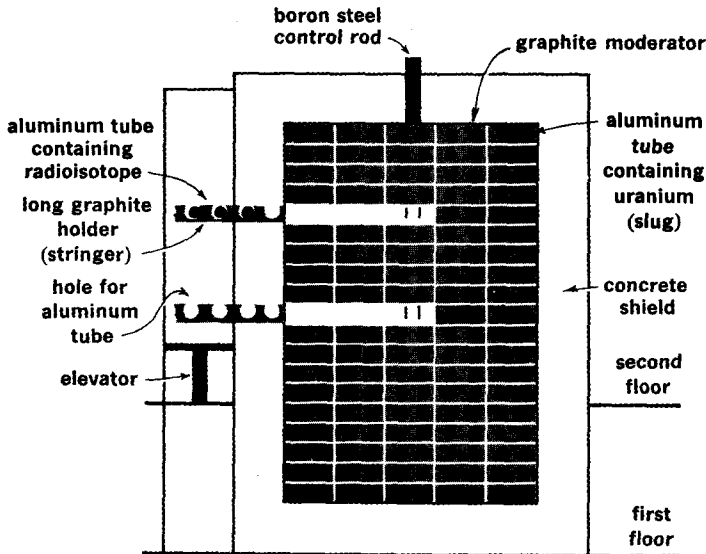


FIG. 15-4

Schematic representation of a cross section of the X-10 reactor.

the moderator, because it slows down the neutrons produced by the fission of uranium. Slow-moving (thermal) neutrons are more apt to be captured by  $^{235}\text{U}$  nuclei and produce fission (Fig. 15-5).

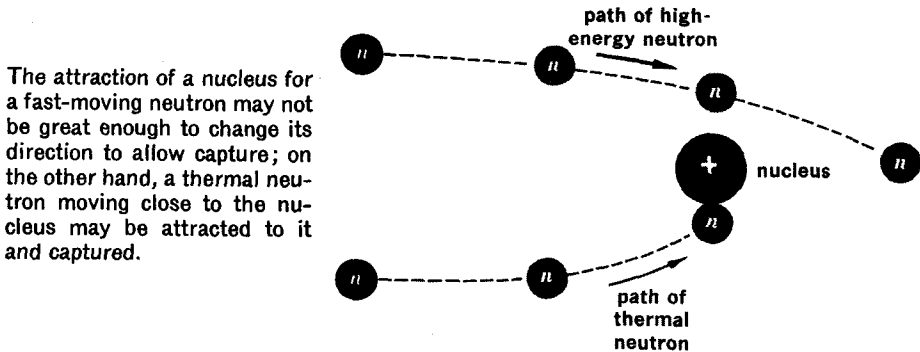


FIG. 15-5

The attraction of a nucleus for a fast-moving neutron may not be great enough to change its direction to allow capture; on the other hand, a thermal neutron moving close to the nucleus may be attracted to it and captured.

2. The graphite bricks are constructed so that open channels exist through the reactor. The uranium (35 tons) in the form of cylindrical slugs is pushed into these channels. Because the X-10 and Hanford reactors use natural uranium, the reactors must be quite large to contain a critical mass.

3. During operation of the reactor,  $^{235}\text{U}$  atoms capture neutrons and fission, thus releasing more neutrons to sustain the fissioning process. Because an excess of neutrons results,  $^{238}\text{U}$  atoms capture



some of these neutrons and then change by beta decay to neptunium and plutonium.

4. The heat liberated by these nuclear changes is removed by an air flow through the reactor at the rate of 100,000 ft<sup>3</sup>/min. This flow of air holds the temperature of the uranium slugs at about 280°C. No effort was made to utilize the heat energy produced by the X-10 reactor. The warm air, after filtration to remove radioactive fission products, was released to the atmosphere.

5. Two kinds of rods, cadmium encased in steel and special boron steel, are mounted so that they can be dropped into vertical holes or pushed into horizontal holes in the reactor cube. Both cadmium and boron steel are efficient neutron absorbers. If the rate of fission becomes too high, these control rods are inserted into the core of the reactor, where they absorb some neutrons and thus slow down the chain reaction.

After the war, the X-10 reactor was used principally for the production of radioisotopes by neutron bombardment. Different elements were placed in some of the hollow channels in lieu of the uranium slugs. The intense neutron bombardment to which they were subjected produced radioactive isotopes. The X-10 reactor is now considered obsolete and was placed in stand-by operation in 1963.

## PRODUCTION OF ENERGY

*Energy and Our Standard of Living.* The United States, with 6 per cent of the world's population, uses one-third of the world's total energy production. This large consumption of energy, of course, makes possible our very high standard of living. Today the average American, with his automobile, power mower, electrical household appliances, and his purchasing power for machine-produced commodities, has the equivalent of several hundred "slaves" working for him. He may live more comfortably than the kings of ancient times.

The world's energy needs are increasing at a very fast rate. For example, the consumption of electrical energy in the United States has been doubling every eight years. It is estimated that by the year 2000 the world's population will have doubled and that the energy consumption will be about five times the present consumption.

The world's present energy production is based on the fossil fuels (coal, oil, and natural gas) that account for about 93 per cent of the energy produced. The labor of man and domestic animals, and water power, account for most of the remainder. How long the fossil fuels will last is a question that cannot be definitely answered. Many people think that they will be exhausted in another century. Therefore, most of the industrial nations of the world are now looking to the fission reaction, carried out in a nuclear reactor, as a means of supplementing the power produced by burning fossil fuels. The experimental reactors built immediately after World War II in the United States

to produce electrical power could not compete in cost per kilowatt hour with the production of electricity by burning coal and oil. Economy of plant production and operation has now advanced to the stage where nuclear power could be competitive with fossil fuels for producing electrical power in localities to which coal has to be hauled some distance, perhaps 60 per cent of this country. In 1964, the nuclear power capacity in the United States was about 1 billion watts. According to United States Atomic Energy Commission estimates, about one-half of the electrical power consumed in the United States will be produced by nuclear power in the year 2000. Great Britain, a leader in nuclear power production, expects to produce 12 per cent of its total electrical power needs in 1969 with nuclear reactors.

*Nuclear Reactors for the Production of Power.* The principles involved when a reactor is operated to produce electrical power are quite simple. An arrangement of uranium, or uranium and thorium, with moderator and control rods, supplies heat energy, as described in the preceding section on the Oak Ridge reactor. This heat energy is carried away by circulating a coolant, such as water, molten sodium, or carbon dioxide, through the reactor. The coolant gives up the heat in a heat exchanger to water, which is converted to steam. The steam in turn operates turbogenerators in the conventional manner to produce electricity.

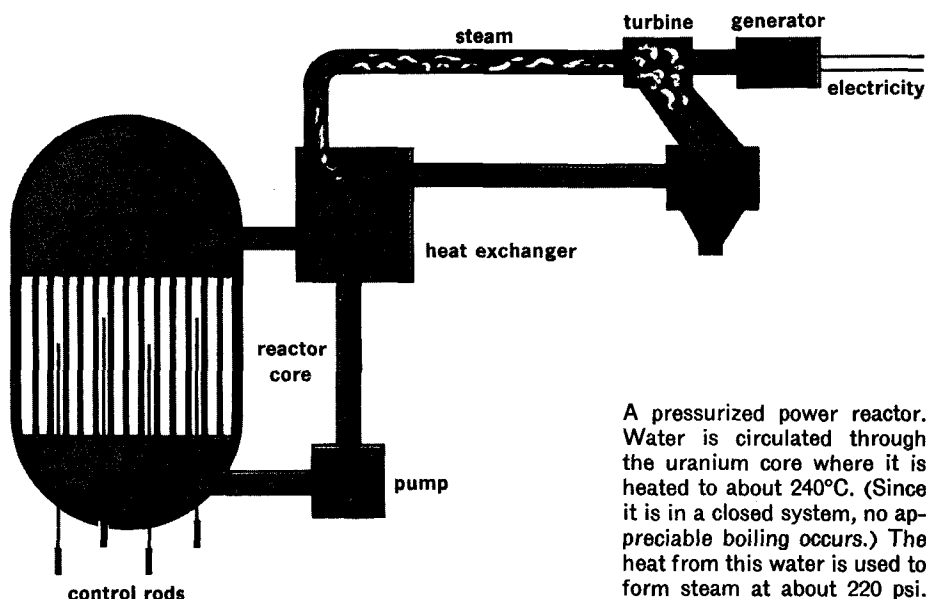
Although graphite is used as the moderator in the gas-cooled ( $\text{CO}_2$ ) reactors that have been built in Great Britain, and in the molten sodium-cooled reactors in this country, ordinary water (or in some cases, heavy water) serves as both moderator and coolant for most reactors now producing power in the United States.

The reactor is controlled by inserting and withdrawing one or more control rods, usually of cadmium. Enough neutrons are absorbed so that on the average only one neutron from a given fission produces a second fission. Under these conditions, the chain reaction is self-sustaining, and the reactor is said to be *critical*. At the critical stage, all through the fissionable fuel, nuclei are fissioning at a fairly regular rate, with the liberation of much energy. The number of nuclei that fission in a unit of time, and hence the power level of the reactor, are determined by the total amount of uranium present, by the ratio of  $^{235}\text{U}$  to  $^{238}\text{U}$ , and by reactor design.

After operating at the critical stage for several months, the reactor fuel becomes poisoned with fission products to such an extent that it must be removed. The fuel is then chemically processed to recover unreacted fissionable material.

Figure 15-6 shows schematically how the energy from the pressurized water reactor is converted to electricity. The United States now has dozens of submarines powered by pressurized water reactors that are fueled with  $^{235}\text{U}$ -enriched uranium. Other types include boiling-water reactors, sodium-cooled, graphite-moderated reactors;

## APPLICATIONS OF NUCLEAR REACTIONS



A pressurized power reactor. Water is circulated through the uranium core where it is heated to about 240°C. (Since it is in a closed system, no appreciable boiling occurs.) The heat from this water is used to form steam at about 220 psi.

FIG. 15-6

gas-cooled, graphite-moderated reactors; homogeneous reactors in which the fuel (uranium compounds) is in solution; and breeder reactors. (See also Table 15-1.)

**BREEDER REACTORS.** A reactor fueled with ordinary uranium makes new fissionable material as it uses up its fissionable  $^{235}\text{U}$ , a process called *breeding*. Breeding occurs because some of the neutrons produced by the fission are captured by  $^{238}\text{U}$  nuclei, thereby setting up the series of reactions that produce  $^{239}\text{Pu}$ , a fissionable material (see page 385). An ideal situation for reactor economy is for each fission to produce two effective neutrons: one causes another fission and one starts the change of  $^{238}\text{U}$  to  $^{239}\text{Pu}$ . To accomplish this, the neutron yield per fission has to be more than two, because a sizeable number of neutrons are taken up by processes that do not result in either fission or breeding. The neutron yield per fission by thermal neutrons for  $^{235}\text{U}$  and  $^{239}\text{Pu}$  is 2.07 and 2.08, respectively, too few to keep the fissioning going and at the same time produce new fuel at the rate the original fuel is being used up. The key to this problem appears to be the development of reactors in which moderators are not used to slow down high-energy neutrons; compared with thermal neutrons, fast neutrons give a higher neutron yield per fission: 2.18 and 2.74, respectively, for  $^{235}\text{U}$  and  $^{239}\text{Pu}$  (Fig. 15-7).

Two experimental breeder reactors built by AEC in Idaho have achieved breeding by a ratio slightly greater than unity. The large Enrico Fermi reactor in Michigan, with a capacity power rating of 90 million watts, is a fast-breeder, sodium-cooled reactor. The inner portion of the fuel component contains uranium enriched with 25

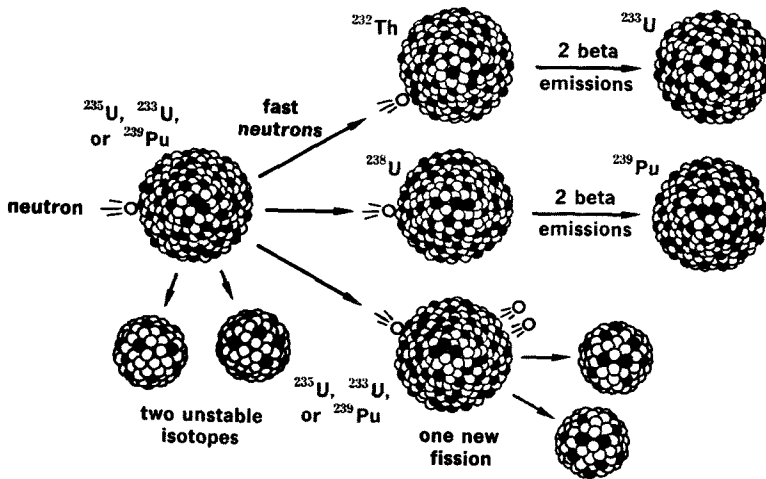


FIG. 15-7

Schematic representation of the production of fissionable material in a breeder reactor.

### Representative reactors

TABLE 15-1

name	fuel	moderator	coolant	purpose
Dresden Power Station, Dresden, Ill.	$\text{UO}_2$ , 1.5% $^{235}\text{U}$	water	boiling water	electric power, 200,000 kw
PWR, Shippingport, Pa.	$\text{UO}_2$ and $^{235}\text{U}$ in U-Zr	water	pressurized water	electric power, 60,000 kw
SGR, Hallam, Neb.	3.6% $^{235}\text{U}$ in Mo alloy	graphite	sodium	electric power, 75,000 kw
Calder Hall A, Great Britain	natural uranium	graphite	carbon dioxide	electric power, 45,000 kw
VVPR1, U.S.S.R.	2% $^{235}\text{U}$ in $\text{UO}_2$	water	pressurized water	electric power, 210,000 kw
NRU, Chalk River, Canada	U	heavy water	heavy water	research, materials testing, isotope production

per cent  $^{235}\text{U}$ , and the outer part or blanket is made of uranium with a depleted  $^{235}\text{U}$  content (0.4 per cent instead of the 0.7 per cent in natural uranium).

### FUSION REACTIONS

In Chap. 14 we noted that matter is converted into energy when certain small atoms fuse to make new atoms. For example, in the fusion of 4 hydrogen atoms to form 1 helium atom, 0.7 per cent of the

## APPLICATIONS OF NUCLEAR REACTIONS

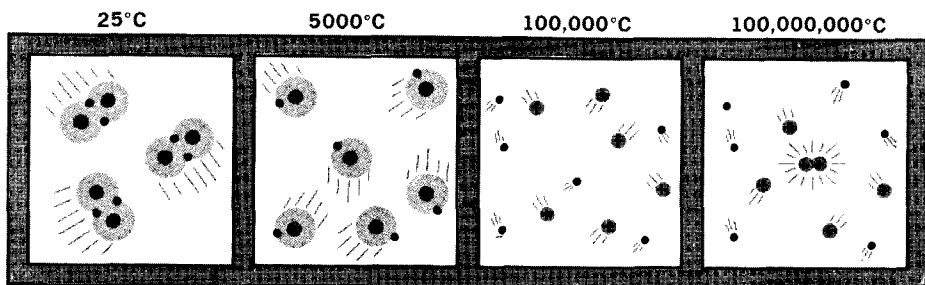
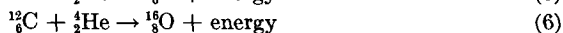
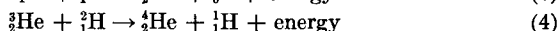
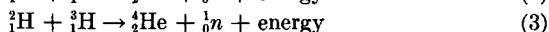
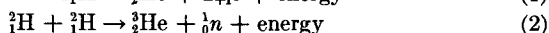
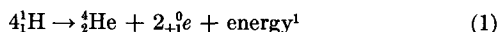


FIG. 15-8

At 25°C deuterium is in the form of diatomic molecules; at 5000°C the diatomic molecules have dissociated into deuterium atoms. At a temperature of 100,000°, kinetic energies are so great that atomic forces no longer hold the electron and the nucleus in the form of a deuterium atom. They move about independently at tremendous velocities. The material is now referred to as deuterium plasma. However, even at this temperature, collisions between nuclei do not effect fusion. At temperatures of 100,000,000°, some nuclei have enough kinetic energy to overcome the repulsion of like charges, and fuse.

mass is converted into energy. In the fission process, 0.1 per cent of the mass of a uranium-235 atom is converted into energy. The following are several examples of fusion reactions that release energy:

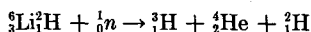


Reactions such as these may take place spontaneously when the temperature is of the order of 100 million degrees or more. At these high temperatures, atoms do not exist as such; instead, there is a plasma of nuclei and of electrons (Fig. 15-8). In this plasma, nuclei merge or interact. Fusion reactions that take place due to high temperatures are often referred to as *thermonuclear* reactions.

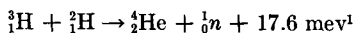
**Stellar Energy.** Spectroscopic examination of the light from the sun indicates that extremely large amounts of hydrogen and helium are present in its atmosphere. The fusion of hydrogen-1 to helium—reaction (1) above—is thought to be the overall reaction which is taking place and which is responsible for the tremendous amount of energy released by the sun. This emission of energy results in a loss in weight of the sun of  $5 \times 10^6$  tons per second.

<sup>1</sup> The positron,  $\text{}^0_{+1}\text{e}$ , is a subatomic particle with the same mass as an electron but a unit positive charge. On the average, a positron exists for only  $1 \times 10^{-8}$  second before colliding with an electron and turning into energy.

**Hydrogen Bombs (Thermonuclear Bombs).** Thermonuclear reactions, such as those in (1), (5), and (6) above, take place slowly at stellar temperatures. Reaction (3), involving tritium, takes place very rapidly at temperatures that can be produced by a fission bomb composed of uranium-235 or plutonium. However, tritium ( $t_{1/2} = 12$  years) is difficult to produce and store. One type of hydrogen bomb depends on the production of tritium in the bomb. In this type, lithium deuteride ( ${}^6\text{Li}^2\text{H}$ , a solid substance) is placed around an ordinary  ${}^{235}\text{U}$  or  ${}^{239}\text{Pu}$  fission bomb. The fission bomb is set off in the usual way. Lithium-6 absorbs some of the neutrons produced and splits into tritium and helium-4:



The temperature reached by the fissioning of  ${}^{235}\text{U}$  or  ${}^{239}\text{Pu}$  is sufficiently high to bring about the fusion reaction of tritium and deuterium:



The largest nuclear bomb exploded to date, a Russian one, was a 60-megaton fission-fusion bomb. A 20-megaton bomb usually contains about 300 lb of lithium deuteride as well as a considerable amount of plutonium and uranium.

**Thermonuclear Power.** We have seen that the fission reaction can be carried out in nuclear reactors so that the large amount of energy released can be put to peaceful purposes, such as the production of electricity. So far, man has been unable to control the fusion reaction in a similar way, although the United States, Great Britain, Russia, and other countries to a lesser extent, have already contributed a good deal of research effort to this end and continue to do so. The maintaining of the very high temperature necessary for the reaction is the chief stumbling block (see Fig. 15-8). Most of the research work has been based on the fusion of deuterium. Even though deuterium is present in natural waters to the extent of only 1 part in about 7,000 parts of hydrogen, it has been estimated that the oceans contain enough deuterium to supply the world at its present energy consumption rate for a trillion years.

## APPLICATIONS TO RESEARCH

The use of radioactivity in research has become commonplace. All the fields of science—chemistry, physics, biology, botany, agriculture, engineering, astronomy, geology, medicine—have felt the impact of new methods made possible by an understanding of nuclear changes

<sup>1</sup> When the energy of a reaction is expressed in electron-volts, the amounts of reactants and products shown in the equation are to be interpreted as individual particles rather than mole quantities.

and the availability of radionuclides. We shall cite only a few examples.

**Dating. AGE OF THE EARTH.** A fascinating calculation based on the concept of half-lives is the probable age of the earth. As shown in Table 17-2, the end product of the uranium-238 decay series is stable lead-206. In nature, where lead-206 and uranium-238 are found together in certain minerals, it is assumed that the lead has been formed as the result of radioactive decay during the passage of many years. The amounts of uranium and lead present can be determined by chemical analysis. On the basis of a knowledge of the half-lives of all the intermediate elements involved,<sup>1</sup> one can calculate the time required to establish the uranium-to-lead ratio found in the minerals.

Such calculations indicate that many rocks have existed in much their present state for billions of years. These and other studies support the theory that the earth is at least 4 to 6 billion years old.

Let us look at an approximation of the age of a uranium ore based on analytical data. An analysis of a sample of uranium ore showed that it contained 0.277 g of <sup>206</sup>Pb and 1.667 g of <sup>238</sup>U. If we assume that all the <sup>206</sup>Pb came from the decay of <sup>238</sup>U, the weight of <sup>238</sup>U that has changed to <sup>206</sup>Pb is

$$\frac{238}{206} \times 0.277 \text{ g} = 0.319 \text{ g of } ^{238}\text{U changed to } 0.277 \text{ g of } ^{206}\text{Pb}$$

The weight of <sup>238</sup>U originally present was

$$1.667 \text{ g of } ^{238}\text{U} + 0.319 \text{ g of } ^{238}\text{U} = 1.986 \text{ g of } ^{238}\text{U (originally present)}$$

In one half-life, one-half of the original 1.986 g, or 0.993 g, of <sup>238</sup>U decays. Because the amount that has decayed is 0.319 g, we can say that the age of the ore is approximately <sup>0.319</sup>/<sub>0.993</sub> half-life:

$$\frac{0.319}{0.993} \times 4.5 \times 10^9 = 1.5 \times 10^9 \text{ years}$$

This ore, about 1.5 billion years old, possibly is sedimentary material formed long after the oldest igneous rocks.

Old rocks found in Finland and Canada give ages of about  $3 \times 10^9$  years. The oldest rocks yet found on earth are from St. Paul's Rocks, tiny islands near the equator in the mid-Atlantic. There is reason to

<sup>1</sup> For ordinary calculations, one needs consider only the half-life of <sup>238</sup>U, because the next longest-lived member (<sup>234</sup>U) has a half-life of  $2.4 \times 10^5$  years, only about 1/10,000 of the <sup>238</sup>U half life (see Fig. 14-6). The amount that exists as <sup>234</sup>U, <sup>226</sup>Ra, and other members of the series at any one time is relatively negligible.

<sup>2</sup> Note carefully that the decay of a radioactive substance does not follow a straight-line or direct-proportion relationship. We have used such a relationship here merely to make a rough approximation (which is in error by about 30 per cent). For a discussion of a more precise method of completing this calculation, see W. B. Guenther, *J. Chem. Educ.*, **35**:414 (1958).

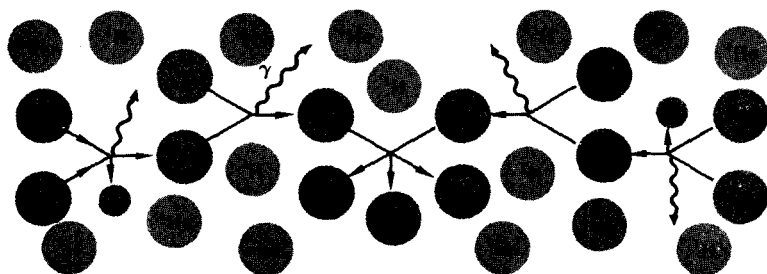


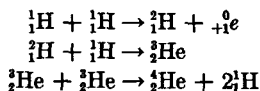
FIG. 15-9

Hydrogen fusion in the sun. The proposed sequence in effect converts four  ${}^1\text{H}$  atoms into a  ${}^4\text{He}$  atom.

believe that the rocks comprising these islands are a part of the earth's mantle (see Chap. 29), having been brought to the surface where the crust is thin by crust and mantle movement. In any event, these rocks are  $4.5 \times 10^9$  years old, as indicated by the  ${}^{87}\text{Sr}$ - ${}^{86}\text{Sr}$  ratio. Both these isotopes are stable; the latter is assumed to have been present when the rock originally formed on cooling, but the  ${}^{87}\text{Sr}$  is formed by the decay of  ${}^{87}\text{Rb}$ , which has a half-life of  $4.6 \times 10^{10}$  years. A similar determination of the age of meteorites indicates the age of planets and the earth of about  $4.5 \times 10^9$  years. Other pairs of parent-product substances used in dating minerals and meteorites include  ${}^{40}\text{K}$ - ${}^{40}\text{Ar}$ , and  ${}^{232}\text{Th}$ - ${}^{208}\text{Pb}$ .

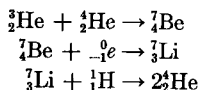
**AGE OF STARS.** The emission spectra of stars provide the basis for formulating theories about their composition, surface and interior temperatures, rate of energy emission, etc. The sun, one of a galaxy of billions of stars, is thought to have a surface temperature of  $6000^\circ\text{K}$ , an interior temperature of  $15,000,000^\circ\text{K}$ , an energy emission of  $4.0 \times 10^{33}$  ergs/sec, and to be composed of approximately 80 per cent hydrogen, 20 per cent helium, and about 1 per cent of all other elements, with carbon, oxygen, and nitrogen making up most of this small fraction.

At  $15,000,000^\circ\text{K}$ , the average kinetic energy of protons ( ${}^1\text{H}$ ) is too small for most of the nuclear collisions to result in fusion, owing to the repulsion of similarly charged particles; but a small number of protons that have higher energies may fuse, so that the fusion of hydrogen in the sun takes place at a slow rate. The sequence of reactions that occurs to convert hydrogen into helium is not known with certainty, although plausible pathways have been proposed that are consistent with laboratory experiments and the energy emission, temperature, and composition of the sun. The following equations show one sequence that has gained considerable support (see Fig. 15-9):





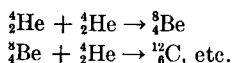
Side reactions, such as those shown below, may occur:



Calculations based on the rate of hydrogen fusion and the amount of hydrogen present indicate that the present rate of hydrogen fusion in the sun will continue for several billion years.

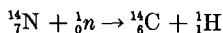
A method of dating the age of a young star, such as the sun, is based on the theory that a young star is relatively rich in lithium and that the lithium tends to decrease rapidly after most of the hydrogen has been consumed. The evidence indicates that the sun is already several billion years old, although it is a young star.

In the red giant stars, spectroscopic examination shows relatively little hydrogen remaining. Presumably, these are older stars, and most of the hydrogen has already been converted to helium to form a helium core. The gravitational contraction of the helium core gives rise to interior temperatures of the order of  $100,000,000^\circ\text{K}$ , so that the fusion of helium is then possible:



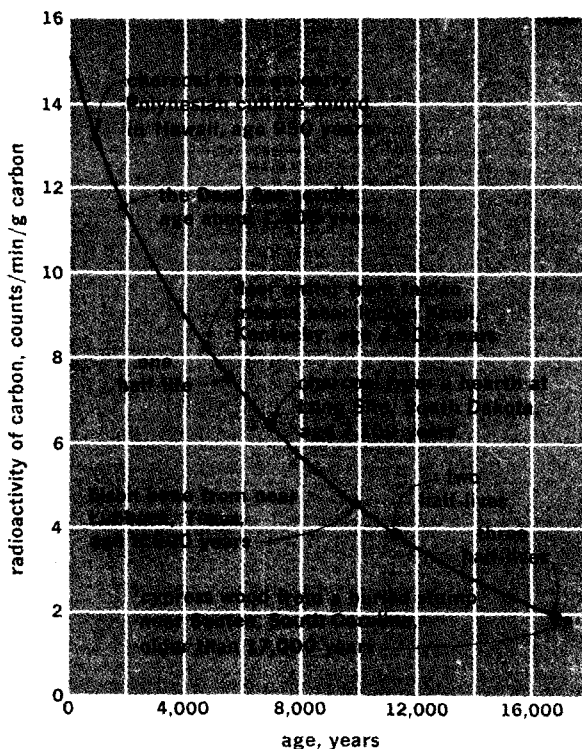
It is estimated that the helium fusion will require 10 billion to 100 billion years. Presumably, another contraction and increase in temperature will occur, and the synthesis will continue with nuclides of high binding energy, such as iron, as the end products.

**AGE OF ORGANIC MATERIALS.** An interesting method of dating ancient objects of an organic nature is based on the fact that the preserved object, if not too old, contains a measurable amount of radioactive carbon-14. Carbon-14 is present in the atmosphere (as  $^{14}\text{CO}_2$ ) in a constant small amount, because it is continually being produced by cosmic ray activity that results in neutron capture by a nitrogen atom and the subsequent expulsion of a proton:



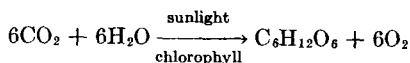
Therefore, at all times a constant, small quantity of  $^{14}\text{CO}_2$  is available to growing plants. Once the growing process stops and carbon-14 is no longer taken up by the plant, the amount of it in the plant tissues begins to diminish through radioactive decay. By measuring the radioactivity due to carbon-14 in living wood and comparing this to the radioactivity in preserved wood or charcoal, we can calculate from the known half-life of carbon-14 (5,600 years) the time that must have elapsed to reduce the radioactivity to that of the preserved object. The interesting dates in Fig. 15-10 have been determined in this manner.

Radiocarbon dating. The amount of  $^{14}\text{C}$  activity remaining in the preserved object is determined. The age is then read from the half-life curve. (The data shown here are from W. F. Libby, *Radiocarbon Dating*, University of Chicago Press, 1954.)



**Mechanism of Chemical Reactions.** Ordinary chemical equations show only the reactants and products. For example, the photosynthesis equation

FIG. 15-10



simply states that carbon dioxide and water react under the conditions shown to form glucose sugar and oxygen. It is highly improbable that six molecules of carbon dioxide and six of water could, under any circumstances, come together simultaneously and interact to form one molecule of glucose and six of oxygen. Most complex reactions such as this one are believed to proceed through a series of changes involving one or two particles at a time. The use of radioisotopes as tracers to follow the course of such reactions has proved an invaluable tool. In the case of photosynthesis, Melvin Calvin and his associates at the University of California used  $^{14}\text{CO}_2$  to solve the very complicated course of this reaction. In this type of work, one uses detection devices, such as a Geiger counter, to follow the radioactive atoms through the various intermediates to the final product.

Many chemical and biochemical processes are now studied, either in test tubes and beakers or in live animals and plants, via radio-

## APPLICATIONS OF NUCLEAR REACTIONS

isotopes, such as  $^{14}\text{C}$ ,  $^{15}\text{N}$ ,  $^3\text{H}$ ,  $^{24}\text{Na}$ . Table 15-2 lists several radioisotopes of common elements that are available for research purposes.

TABLE 15-2 *Isotopes available as radiotracers*

radioactive isotope	emission	half-life
hydrogen-3 (tritium)	beta	12.46 years
carbon-14	beta	5,600 years
sulfur-35	beta	$1 \times 10^8$ years
chlorine-36	beta	14.3 days
phosphorus-32	beta	15 hours
sodium-24	beta, gamma	14.8 hours
iron-59	beta, gamma	4.51 days

**Medicine.** One of the most widely publicized applications of radioactive isotopes is in the treatment of disease in plants and animals. Beta and gamma emitters, such as cobalt-60 and cesium-137, are used to irradiate diseased portions of living tissue in much the same way that X rays have long been employed. Some 200 gamma-ray teletherapy units are now in use in medical institutions in this country. Radioactive radiation is often more effective than X rays, because its action can be limited to the afflicted tissue more easily, thus preventing radiation damage to healthy tissue. For example, radioactive iodine is used in the treatment of diseased thyroid glands, radioactive phosphorus in cancer of the bone, and radioactive sodium (in capsules) in localized malignancies.

**Promotion of Chemical Reactions.** Many chemical reactions that serve for the commercial production of common substances proceed through one or more difficult steps that require elevated temperatures, catalysts, and other special conditions. Several of these reactions are now being studied experimentally with the objective of using ionizing radiation to activate the molecules, thereby avoiding the use of heat energy, catalysts, and such conditions. Fission products from nuclear reactors are one source of ionizing radiation; electron-accelerating machines are another. There is considerable evidence that many commodities can be produced more economically by radiation-induced reactions. Already, one United States company is producing 500 tons annually of ethyl bromide ( $\text{C}_2\text{H}_5\text{Br}$ ) in a process using cobalt-60 radiation, and several companies are using radiation to effect cross-linking of polyethylene (see Chap. 28). Russia reports using fission-product radiation to make phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) from benzene ( $\text{C}_6\text{H}_6$ ) and water. Japan uses radiation to effect the formation of polyvinyl resins.

**Miscellaneous.** Radiation is used in a variety of commercial processes, including manufacture of semiconductors (radiation creates

a controlled number of imperfections in the crystal lattice); goat hair sterilization (2,250 tons annually for carpet manufacture); sterilization of surgical sutures (80 per cent of the United States market); sprout inhibition of potatoes (500 tons per year in Canada); food sterilization (experimental stabilization of military rations—chicken, beef, pork, and ham); and grafting dye-sites to polypropylene.

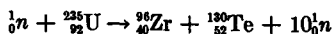
## CHAPTER REVIEW

### Terms

Critical mass, chain reaction, fission bomb, megaton, fall-out, fissionable, nuclear reactor, thermal neutrons, moderator, control rod, nuclear power, breeder reactor, fusion bomb, stellar energy, positron, thermonuclear power, radioactive dating.

### Exercises

1. a. Write a hypothetical equation for the fission of  $^{233}\text{Th}$  as the result of neutron bombardment. Assume that nuclides of cesium and bromine and four neutrons are produced.  
b. Could a reaction, such as that described in (a), be the basis for a chain reaction? Explain.
2. Repeat Exercise 1, using  $^{239}\text{Pu}$  as the fissionable nuclide and changing other species as little as possible.
3. a. Calculate the mass loss per atom of uranium for the following hypothetical fission reaction to yield stable nuclides as products (it is unlikely that so many neutrons would be emitted in any fission):



The weights of the nuclides are  $^{235}\text{U}$ , 235.0439;  $^{95}\text{Zr}$ , 95.9082; and  $^{130}\text{Te}$ , 129.9067.

- b. Using the foregoing hypothetical equation, calculate the weight in grams of uranium that would have to fission to release  $2 \times 10^{13}$  cal, approximately the energy attributed to nuclear bombs like those used in World War II.
- c. Calculate the weight in grams and pounds of uranium needed for a bomb if the fissioning process has an efficiency of only 1 per cent.
4. What happens to the electrons after the nucleus of an atom splits into two smaller nuclei?
5. Consider an isolated  $^{235}\text{U}$  atom, say in a mineral deposit. Could it fission?
6. Although natural uranium contains  $^{235}\text{U}$ , an explosive chain reaction does not develop in uranium ores or in uranium metal. Why?
7. Describe, using hypothetical nuclear equations where helpful, various things that may happen to neutrons in a mass of fissioning uranium.

## APPLICATIONS OF NUCLEAR REACTIONS

8. Neutrons are effective in bringing about nuclear changes when they move at relatively low speeds. How is this behavior taken advantage of in the operation of a nuclear reactor?
9. Professor Henry Margenau has written (*The Nature of Physical Reality*, McGraw-Hill, Inc., New York, 1950, p. 420): "... even though I know the exact state of a neutron (having a sharp energy) that is capable of setting off an atomic bomb, and know precisely the location of the block of plutonium that is ready to be exploded, I cannot predict whether the disaster will occur. The fate of the globe, as a single event, may hide itself within atomic uncertainty." Consider the first sentence in the light of the principles discussed in the chapter, and write a paragraph outlining your conclusions.
10. A fission product that has a neutron-proton ratio of 81:50 is unstable and decays by a series of changes till it attains the stable ratio of 77:54. Identify all the nuclides in this series of changes.
11. How is the fact that fission products are beta emitters rather than alpha emitters related to the observed band of stable nuclei?
12.
  - a. The storage and disposal of fission products from nuclear power plants is a pressing problem. Some have been put deep underground, some have been sunk in concrete containers in the sea. Suggest possible objections to these methods.
  - b. Harmful wastes from ordinary chemical plants are sometimes disposed of by diluting them or by changing them chemically and pumping them into a river or into the sea. Discuss the application of these techniques to fission-product wastes.
13. Suggest possible commercial applications that might make use of the large amount of radioactive materials now accumulating from nuclear power reactors.
14. With certain materials it is possible to construct a nuclear power plant but not a nuclear bomb (not, that is, without highly difficult processing). Explain this with the aid of labeled diagrams.
15. How does the purpose of the moderator differ from that of the control rods in a nuclear reactor?
16. In the type of nuclear power plant that uses circulating solutions of fissionable nuclides, relatively little fissioning takes place in the pipes and conduits through which the solution is pumped, but when a large volume of the solution is collected in the reactor core, fissioning becomes very efficient. Explain, using a diagram.
17. Compare the general technique of producing electrical power by burning coal with that of producing it by a nuclear reactor.
18. Describe the essential nuclear reactions taking place in an ideal breeder reactor in which  $^{239}\text{Pu}$  is the fissionable material. Theoretically, what is the only raw material that must be continually supplied?
19. It is suggested that one use of space rockets would be to dispose of fission products from nuclear power plants. To guard against the possibility

that such a rocket could wander about the universe till it causes some mischief, it would be well to put it on a heavenly body where it could do no harm. Where would you suggest?

20.
  - a. Write a chemical equation for the production of lithium hydride.
  - b. What sort of chemical bond would exist in lithium hydride?
  - c. Would you predict that lithium hydride would be a solid, a liquid, or a gas?
  - d. What would be some of the difficulties of producing isotopically pure  $^6\text{Li}^3\text{H}$ ?
21. One of the methods of dating rocks involves the determination of relative amounts of a radioactive nuclide and a stable nuclide. Another method involves two stable nuclides. Describe these two methods and state any assumptions made in calculating the ages of rocks in these ways.
22.
  - a. Name several elements that are among the heaviest likely to be formed by fusion of two nuclei in stars.
  - b. Suggest a way in which atoms of the highest known mass numbers may be formed in stars.
23. The nuclear reactions of primary interest in the stars are exothermic. Write equations for three such reactions. Write an equation for a possible endothermic nuclear reaction that might take place in a star, and explain how this might come about.
24. The age of an old carbon-containing object is determined simply by the measurement of the present radioactivity of the carbon. How is this procedure the same as, or how does it differ from, the determination of the age of minerals?
25. Construct the decay curve for tritium,  $t_{1/2} = 12.5$  years, similar to the decay curve for  $^{14}\text{C}$  (see Fig. 15-10). Instead of plotting counts per minute per gram versus time, plot the percentage remaining versus time. Start with 100 per cent at zero time, and determine the points for 50 per cent remaining, 25 per cent remaining, etc.
26. Tritium is produced in the atmosphere by cosmic radiation and is carried to the earth's surface by rains. Hence, it is available to growing plants in very small amounts as  $^3\text{H}_2\text{O}$ . Once growth stops, the amount of tritium in a plant steadily diminishes (compare with  $^{14}\text{C}$ ). An old wine from a wine cellar in Paris gave a tritium assay of only 10 per cent of the tritium in living plants. Using the graph constructed in Exercise 25, estimate the age of the wine.
27. Would an assay of the deuterium content of the wine in Exercise 26 provide data that could be used to calculate the age of the wine? Explain.
28. Would a  $^{14}\text{C}$  assay of the wine in Exercise 26 result in a more accurate estimation of the age of the wine than the tritium assay? Discuss fully.
29. Radioactive carbon has proved very useful in establishing dates of activities of prehistoric man, but uranium or tritium is useless for such studies. Why?

## APPLICATIONS OF NUCLEAR REACTIONS

30. Samples of vitamin K, made radioactive by substitution of tritium for hydrogen, have been investigated for possible use in the treatment of cancerous tumors. What advantage might such a method of treatment have over irradiating a tumor with beta radiation? If the vitamin K had an activity of 1 curie per 5 mg, how many beta particles per second would be emitted by 0.001 g of the vitamin?
31. After the theory of nuclear fission had been worked out, a pilot reactor was built (in Chicago), and it functioned the first time it was tried; the subsequent development of power-producing fission reactors proceeded fairly rapidly and smoothly. In contrast, a great deal of effort has been expended in the attempt to produce a controlled nuclear fusion, but with little success to date. How do you account for this?

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## THERMOCHEMISTRY



The study of the changes in heat energy that accompany chemical reactions is called **thermochemistry**. The subject is of fundamental importance, not only because we often want to know how much energy can be obtained from reactions, but also because certain theories relative to the chemical bonding and structures of substances are based on the study of energy changes.

## ENTHALPY

## HESS'S LAW

In Chap. 5 the measurement of the heat evolved or absorbed during a chemical reaction was described. The technique of determining these enthalpy changes involves the careful use of calorimeters, a skill developed by Lavoisier and other early chemists and refined to extreme precision today in such laboratories as the National Bureau of Standards. It was in 1840 that the Swiss-Russian chemist G. H. Hess stated one of the most useful generalizations of thermochemistry. A modern version of Hess's law is, *for a given overall reaction, the change in enthalpy is always the same, whether the reaction is performed directly or whether it takes place indirectly and in different steps.*

As an example of Hess's law, consider the exothermic reaction between sulfur and oxygen to produce sulfur dioxide, followed by the exothermic reaction between sulfur dioxide and more oxygen to produce sulfur trioxide:



<sup>1</sup> As indicated in Chap. 5, most changes in enthalpy cited in this text are for processes in which the initial and final states are 25°C and 1 atm.

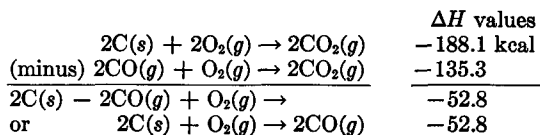


If these two steps are considered to take place as a simple one-step overall reaction, the heat evolved is the sum of the two steps:



It will be recalled that the enthalpy change during a reaction,  $\Delta H$ , refers to a change in heat content of a system of chemicals due to a chemical reaction. In each of the three reactions just described, the product has a smaller heat content than the reactants, hence the decrease in heat content is shown by the minus sign. The heat lost by the chemicals is given off to the surroundings in the exothermic reaction.

One useful consequence of Hess's law is that thermochemical equations can be added or subtracted to produce data that are difficult to determine experimentally. For example, carbon and carbon monoxide are important commercial fuels; therefore, it is of interest to compare the amount of heat liberated when carbon is burned to carbon dioxide with the amount of heat liberated when carbon is burned to carbon monoxide. The latter enthalpy change or heat of reaction is difficult to determine, because carbon monoxide is burned more readily than carbon. Consequently, a reaction in which carbon is burned in the theoretical amount of oxygen needed to form carbon monoxide produces a mixture of carbon dioxide, carbon monoxide, and unburned carbon. However, we can calculate the heat of combustion of carbon to carbon monoxide by determining the heat of combustion (1) of carbon to carbon dioxide and (2) of carbon monoxide to carbon dioxide. Subtracting the thermochemical equation for the latter reaction from that of the former gives the desired information:



## STANDARD ENTHALPIES

Let us look again at the reaction between carbon and oxygen to yield carbon dioxide. The fact that this reaction is exothermic can be explained by assuming (1) that each of the three substances has its own characteristic heat content or enthalpy,  $H$ , and (2) that the sum of the enthalpy of carbon plus that of oxygen is greater than the enthalpy of carbon dioxide. When the enthalpy of the reactants is greater than that of the products, a reaction is exothermic, as discussed in Chap. 5.

$$\Delta H_{\text{reaction}} = (H_{\text{product 1}} + H_{\text{product 2}} + \dots) - (H_{\text{reactant 1}} + H_{\text{reactant 2}} + \dots)$$

$$\Delta H_{\text{reaction}} = \Sigma H_{\text{products}} - \Sigma H_{\text{reactants}}$$

**Arbitrary Assignment of Standard Enthalpies.** The enthalpy of a substance is an example of a **state function**, a function that depends only on the present state of the substance and not on the path by which its present state was attained. In the example of sulfur trioxide referred to previously, at 25°C and 1 atm the sulfur trioxide has 94.45 kcal/mole less enthalpy than the elements from which it is composed. This change in enthalpy is definite; it makes no difference whether the sulfur trioxide is formed from the elements directly or in two steps, nor whether the oxygen was obtained from the atmosphere or by the electrolysis of water, nor whether the sulfur was found as the element near the Texas coast or was melted out of volcanic rocks in Sicily.

The absolute enthalpies of substances are not specified, but it is easy to determine relative values of enthalpies by measuring the  $\Delta H$  of a reaction precisely and by choosing an arbitrary standard for comparison. The standard agreed on is that the relative enthalpies of the elements<sup>1</sup> are zero at 25°C and 1 atm pressure. The relative enthalpies of other physical and chemical states are compared to this standard. Enthalpy changes at 25° and 1 atm are called *standard changes* and are symbolized by  $\Delta H^\circ$ . Most of the enthalpy data given in this chapter and earlier in the text are at or near standard conditions. The symbol  $\Delta H$  is used if it is not important to emphasize standard conditions or if the data do not refer precisely to standard conditions.

By measuring the  $\Delta H^\circ$  values for many reactions involving elements, standard enthalpies of formation of compounds,  $\Delta H_f^\circ$ , can be determined. For example, in the case of sulfur trioxide, the value -94.45 kcal/mole is not the absolute enthalpy of sulfur trioxide at 25°C and 1 atm, but it is the enthalpy of the compound as compared with the enthalpies of the elements under these conditions. To show the result of arbitrarily assigning a relative heat content of zero to elements at the standard state, consider again the reaction



$$\Delta H \text{ reaction} = \Sigma H \text{ products} - \Sigma H \text{ reactants}$$

$$-94.45 \text{ kcal} = H \text{ product} - (0 + 0)$$

$$H \text{ product} = -94.45 \text{ kcal} = \Delta H_f^\circ \text{ of SO}_3$$

For the special case involving the reaction of elements, the heat of reaction is the heat of formation of the compound produced. The *standard enthalpy of formation of a substance*,  $\Delta H_f^\circ$ , is defined as the change in heat content when the substance is formed from its elements at standard conditions. Thousands of such standard enthalpies of formation have been measured or calculated; a few representative ones are listed in Table 16-1.

<sup>1</sup> If the element exists in more than one form, zero enthalpy is assigned to the most stable allotrope. In the case of oxygen, for example, ordinary oxygen is assigned zero enthalpy; ozone has a relative heat content greater than zero.

TABLE 16-1 *Enthalpies of formation,  $\Delta H_f^\circ$ , kcal/mole at 25°C and 1 atm*

substance	$\Delta H_f^\circ$	substance	$\Delta H_f^\circ$
AgCl(s)	- 30.36	HBr(g)	- 8.66
AgCN(s)	34.94	HCl(g)	- 22.06
B <sub>2</sub> H <sub>6</sub> (g)	7.5	HF(g)	- 64.2
BrCl(g)	3.51	HN <sub>3</sub> (g)	70.3
CH <sub>4</sub> (g)	- 17.89	H <sub>2</sub> O(l)	- 68.32
C <sub>2</sub> H <sub>2</sub> (g)	54.19	H <sub>2</sub> O(g)	- 57.80
C <sub>2</sub> H <sub>4</sub> (g)	12.50	H <sub>2</sub> O <sub>2</sub> (l)	- 44.84
C <sub>2</sub> H <sub>6</sub> (g)	- 20.24	ICl(g)	4.20
C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> (s)	-302*	LiF(s)	-146.3
C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> (s)	-531*	NH <sub>3</sub> (g)	- 11.04
CO(g)	- 26.42	NH <sub>4</sub> NO <sub>3</sub> (s)	- 87.27
CO <sub>2</sub> (g)	- 94.05	NaCl(s)	- 98.2
ClF(g)	- 13.3	NaCl(aq)	- 97.3
C <sub>3</sub> H <sub>5</sub> (NO <sub>3</sub> ) <sub>3</sub> (l)	- 84*	SO <sub>2</sub> (g)	- 70.96
CaO(s)	-151.9	SO <sub>3</sub> (g)	- 94.45
CaCO <sub>3</sub> (s)	-288.5	ZnCl <sub>2</sub> (s)	- 99.40
Fe <sub>2</sub> O <sub>3</sub> (s)	-196.5	Zn(CN) <sub>2</sub> (s)	18.4

\* Calculated, at 20°C, from data in *Handbook of Chemistry and Physics*, Hodgman, C. E., (ed.), The Chemical Rubber Publishing Co., Cleveland, 1961.

SOURCE: Data taken mainly from *Circular of the National Bureau of Standards 500*, Washington, 1952.

An examination of Table 16-1 reveals several items of interest. First, we see that when a compound is formed from its elements, the reaction may be either exothermic or endothermic. Compounds formed from their elements in exothermic reactions ( $\Delta H_f^\circ$  is negative) are called exothermic compounds; the others are called endothermic compounds. Endothermic compounds are sometimes unstable. Hydrogen azide, HN<sub>3</sub>, explodes violently when heated, decomposing into hydrogen and nitrogen, with the evolution of 70.3 kcal/mole. Acetylene, C<sub>2</sub>H<sub>2</sub>, is also explosive at room temperature as a pure liquid. It is commercially available as a fuel gas in cylinders as a stable solution in acetone. An endothermic compound, such as acetylene, is a relatively efficient fuel. Because heat is given off as an endothermic compound decomposes, it gives off more heat in its combustion than it would were it an exothermic compound. (See Problem 2, which follows.)

A second generalization that is apparent in Table 16-1 is that an ionic compound usually has a larger negative enthalpy of formation than a covalent compound has. Some covalent compounds, such as HF, are exceptions to this rule, but as a general guide it is sound. Of course, we have to make this comparison in terms of a similar number of atoms involved per mole. The covalent sucrose (table sugar), C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>, with 45 atoms per molecule cannot be compared directly with the ionic lithium fluoride, LiF, with only 2 atoms per unit.

A third item to note in Table 16-1 is that the physical state of a compound may make a considerable difference in its enthalpy. In the

case of water the difference between the gaseous and liquid states is 10.52 kcal/mole. In changing from a gas to a liquid, a substance loses enthalpy equivalent to its heat of vaporization and so has a lower enthalpy in the liquid state.

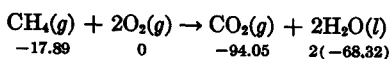
**Standard Enthalpies of Reactions,  $\Delta H_r^\circ$ .** F. D. Rossini, an outstanding thermochemist who has worked at the National Bureau of Standards, has said that "... the aim of thermochemistry is to provide the experimental data for compiling a table of values from which may be calculated the heat of every possible chemical reaction." The data in Table 16-1 are typical of those which can be used to calculate heats of reaction,  $\Delta H_r^\circ$ , for all sorts of reactions, both actual and hypothetical ones. The equation used is similar to one stated previously:

$$\Delta H_r^\circ = \Sigma \Delta H_f^\circ \text{ products} - \Sigma \Delta H_f^\circ \text{ reactants}$$

A few examples will illustrate the method of calculation.

**PROBLEM 1** Calculate  $\Delta H_r^\circ$  for the combustion of methane,  $\text{CH}_4$ .

**Solution** Write a balanced equation for the reaction, and list the  $\Delta H_f^\circ$  values for each substance (Table 16-1):

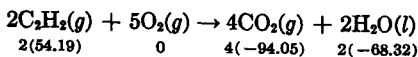


$$\begin{aligned} \Delta H_r^\circ &= \Sigma \Delta H_f^\circ \text{ products} - \Sigma \Delta H_f^\circ \text{ reactants} \\ &= (-94.05 - 136.64) - (-17.89) \end{aligned}$$

$$\Delta H_r^\circ = -212.80 \text{ kcal/mole CH}_4 \text{ burned}$$

**PROBLEM 2** Calculate  $\Delta H_r^\circ$  for the combustion of acetylene,  $\text{C}_2\text{H}_2$ .

**Solution** Write a balanced equation for the reaction, and list the  $\Delta H_f^\circ$  values for each substance:

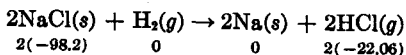


$$\begin{aligned} \Delta H_r^\circ &= (-376.20 - 136.64) - (108.38) \\ &= -621.22 \text{ kcal/2 moles C}_2\text{H}_2 \end{aligned}$$

$$\Delta H_r^\circ = -310.61 \text{ kcal/mole C}_2\text{H}_2$$

**PROBLEM 3** Calculate  $\Delta H_r^\circ$  for the reaction between sodium chloride and hydrogen to give sodium and hydrogen chloride.

**Solution**



$$\begin{aligned} \Delta H_r^\circ &= (-44.12) - (-196.4) \\ &= +152.3 \text{ kcal/2 moles NaCl} \end{aligned}$$

$$\Delta H_r^\circ = +76.1 \text{ kcal/mole NaCl}$$

In all the foregoing problems the value of  $\Delta H_r^\circ$  calculated is the *standard enthalpy of reaction* in going from reactants at 25°C and 1 atm to the products at the same conditions. Changes in heat content

at some other conditions can be calculated starting with standard enthalpies by methods that we shall not take up. However, because the enthalpy change of a chemical reaction at normal room temperature and pressure does not usually differ greatly from the change at 25° and 1 atm, calculations based on the tabulated values of  $\Delta H_f^\circ$  can serve as reliable approximations of heats of reaction under normal conditions.

It is interesting to look back in history and see what conditions were accepted as "standard" at different times. It is convenient to do calorimetric measurements near room temperature, because the calorimeter itself will not be gaining much heat from or losing much heat to its surroundings. Much of the early work was done in the temperate climates of Germany, France, and England in laboratories not well heated. Many of the early workers found it convenient to work at 18°C (about 64°F), and many data are still available at that "standard" temperature. Another temperature used for much tabulated data is 20°C, with the trend in later years, and particularly in the United States, being to 25°C. An ice calorimeter devised by Lavoisier and Laplace worked well only if the room temperature was within 4° of freezing, a working condition to strain the devotion of the most dedicated chemist.

**Enthalpy Changes for Physical Processes.** In actual laboratory practice in measuring the heats of reactions, the scientist may use a calorimeter similar to that shown schematically in Fig. 5-3. With such equipment the reaction is carried out, not at constant pressure, but at constant volume in a small steel bomb. The final pressure in the bomb may be very high if most of the products tend to be gases, and the physical state may differ from that which is stable at constant pressure.

However, from the heat change measured under the condition of constant volume, the chemist can calculate the enthalpy change for the reaction as though it had been carried out in an open container at constant temperature and pressure. To do this, he must consider the heat changes involved in the expansion or compression of gases, in the heating or cooling of substances, and in any solid-liquid-gas transformations. Extensive tables are available of heats of compression, heat capacities (or specific heats), heats of fusion ( $\Delta H_{fus}$ ), and heats of vaporization ( $\Delta H_{vap}$ ) for all sorts of substances under all sorts of conditions. Using these data, measured heat changes for thousands of reactions have been corrected to show what the standard enthalpy change,  $\Delta H_r^\circ$ , would be if the reaction were carried out under the conditions of constant temperature and pressure at 25°C and 1 atm.

**LAW OF DULONG AND PETIT.** A calorimetric study of great historical importance was that reported by the French chemists P. L. Dulong and A. T. Petit in 1819. Their determinations of the specific heats of elements, listed in Table 16-2, led them to state the law,

*Data supporting the law of Dulong and Petit*

TABLE 16-2

element	specific heat	atomic weight (O = 1)	atomic weight $\times$ specific heat	atomic weight (O = 16)	atomic weight $\times$ specific heat
bismuth	0.0288	13.30	0.3830	209	6.0
lead	0.0293	12.95	0.3794	207	6.1
gold	0.0298	12.43	0.3704	197	5.9
platinum	0.0314	11.16	0.3740	195	6.1
tin	0.0514	7.35	0.3779	119	6.1
silver	0.0557	6.75	0.3759	108	6.0
zinc	0.0927	4.03	0.3736	65.4	6.1
tellurium	0.0912	4.03	0.3675	128	11.7
copper	0.0949	3.957	0.3755	63.5	6.0
nickel	0.1035	3.69	0.3819	58.7	6.1
iron	0.1100	3.392	0.3731	55.8	6.1
cobalt	0.1498	2.46	0.3685	58.9	8.8
sulfur	0.1880	2.011	0.3780	32.1	6.0

NOTE: Numerical data in columns 2, 3, and 4 are from the original work (1819). Data in column 5 are modern. Columns  $2 \times 5$  = column 6.

*atoms of all simple substances have the same capacity for heat.* Another way of stating the law is: the product of the specific heat times the atomic weight is a constant. Dulong and Petit used a scale of atomic weights in which oxygen was assigned the weight of unity. Using the data in columns 2, 3, and 4 of Table 16-2, the law can be stated in the form of an equation:

$$(\text{specific heat}) \times (\text{atomic weight}) \simeq 0.375$$

With the later scale of atomic weights based on O = 16 and with more determinations of atomic weights and specific heats, the Dulong-Petit constant was changed to about 16 times 0.375 or 6.0.<sup>1</sup> The law was then stated

$$(\text{specific heat}) \times (\text{atomic weight}) \simeq 6.0$$

Expressed in units:

$$[\text{cal}/(\text{g} \times \text{deg C})] \times [\text{g}/\text{mole}] \simeq 6.0 \text{ cal}/(\text{mole} \times \text{deg C})$$

In this form the meaning of the Dulong-Petit relationship is clear. It takes the same amount of heat ( $\sim 6.0$  cal) to raise the temperature by one degree of  $6.02 \times 10^{23}$  atoms, irrespective of whether the atoms are of gold, lead, silver, or some other element.

Columns 5 and 6 in Table 16-2 show how the relationship applies to modern values of the atomic weights, if the old specific heat values of 1819 are used. Two cases of poor fit are seen immediately in cobalt and tellurium. The modern value of the specific heat of cobalt at room temperature is 0.100 cal/(g  $\times$  deg C), which, multiplied by 58.9, would give 5.9 as a value in Table 16-2 instead of 8.8. The case of tellurium is more interesting, since the old value of 0.0912 for the

<sup>1</sup> Other popular Dulong-Petit "constants" adopted have included 6.2 and 6.4.

specific heat is so different from the modern value of  $0.0483 \text{ cal}/(\text{g} \times \text{deg C})$ . Their poor value for the specific heat of tellurium probably led Dulong and Petit to err and choose 4.03 instead of 8.06 for an atomic weight of tellurium. The latter value agrees well with the modern value:  $(8.06)(16) = 129$  as compared with today's value of 128.

The great use of the law shortly after it was discovered was in calculating approximate atomic weights for some of the little-studied elements. A particularly striking case was that of silver. It was known that 13.52 g of silver combined with 1 g of oxygen, but there was disagreement about the formula of silver oxide. Should it be written  $\text{AgO}_2$  or  $\text{AgO}$  or  $\text{Ag}_2\text{O}$ ? The great Swedish chemist J. J. Berzelius favored the first formula.

Giving an atom of oxygen a weight of 1, a different relative weight for the silver atom could be calculated to agree with each possible formula, as we can show.

For  $\text{AgO}_2$ ,

$$\frac{\text{at. wt Ag}}{2(\text{at. wt O})} = \frac{\text{at. wt Ag}}{2(1)} = \frac{13.52 \text{ g of Ag}}{1 \text{ g of O}}$$

$$\text{at. wt Ag} = \frac{2(13.52)}{1} = 27.04$$

For  $\text{AgO}$ ,

$$\frac{\text{at. wt Ag}}{\text{at. wt O}} = \frac{\text{at. wt Ag}}{1} = \frac{13.52 \text{ g of Ag}}{1 \text{ g of O}}$$

$$\text{at. wt Ag} = 13.52$$

For  $\text{Ag}_2\text{O}$ ,

$$\frac{2(\text{at. wt Ag})}{\text{at. wt O}} = \frac{2(\text{at. wt Ag})}{1} = \frac{13.52 \text{ g of Ag}}{1 \text{ g of O}}$$

$$\text{at. wt Ag} = \frac{13.52}{2} = 6.76$$

When Dulong and Petit discovered the relation between specific heat and atomic weight they were able to choose one of these three possible atomic weights for silver by first calculating the approximate atomic weight from their equation:

$$(\text{specific heat}) \times (\text{atomic weight}) \simeq 0.375$$

or

$$\text{atomic weight} \simeq \frac{0.375}{\text{specific heat}} = \frac{0.375}{0.0557} = 6.75$$

Of the three choices, 6.76 must be the atomic weight of silver, if oxygen is 1. Dulong and Petit chose 6.75 for the weight of silver to list in their table (rather than 13.5 or 27.0), because that weight best fit in with the data for other elements and with their data for silver. In the case of silver their choice has stood the test of time, whereas in the case of tellurium it has not.

Not only does the Dulong and Petit relationship enable a calculation of atomic weights, but of formulas and oxidation numbers, also. In the example of silver oxide, once the atomic weight of silver is chosen as 6.75 (or 6.76), it is seen that silver oxide has the formula  $\text{Ag}_2\text{O}$ , and silver has an oxidation number of +1 in this compound.

On the scale of oxygen = 16 we shall illustrate the usefulness of the Dulong and Petit relationship with another example to show how the relationship was used in a systematic way. Three equations were employed:

$$(\text{specific heat}) \times (\text{approximate at. wt}) = 6.0$$

$$\frac{(\text{approximate at. wt})}{(\text{equivalent wt})} \simeq \text{a small whole number}$$

$$(\text{small whole number}) (\text{equivalent wt}) = \text{precise at. wt}$$

The *equivalent weight* (or combining weight) was defined as the precise weight of an element that combines with 8.000 g of oxygen. The small whole number we call the oxidation number today, but years ago it was called the valence.

Consider the element tungsten, which has a specific heat of 0.034 cal/(g  $\times$  deg C) and an equivalent weight of 30.64 g, as determined by analyzing tungsten oxide:

$$\text{approximate at. wt} = 6.0/0.034$$

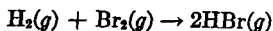
$$= 176$$

$$\frac{(\text{approximate at. wt})}{(\text{equivalent wt})} = \frac{176}{30.64} = 5.7$$

Although 5.7 is not a small whole number, this relationship is approximate, so that it is obvious the number sought must be 6. Therefore, the precise atomic weight of tungsten is  $(6)(30.64) = 183.84$ . The oxidation number of tungsten is 6; the formula for the analyzed oxide of tungsten is  $\text{WO}_3$ .

Although the law of Dulong and Petit was of real use at one time, it was always of limited value. Many elements do not behave in accordance with the law, particularly those of low atomic weight. For instance, the products of specific heat times atomic weight for boron and carbon are 3.3 and 1.4, respectively, near room temperature, instead of 6.0 cal/(mole  $\times$  deg C).

**Enthalpies of Dissociation and Bond Energies.** A type of reaction that is of fundamental importance in interpreting other reactions is the dissociation of molecules. For example, the reaction



probably occurs in a series of steps, one of which may be the breaking of the bond in a molecule of bromine to form two atoms:

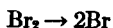




TABLE 16-3     *Dissociation energies,  $\Delta H_{dis}^\circ$ , of diatomic elements, kcal/mole*

reaction	$\Delta H_{dis}^\circ$	reaction	$\Delta H_{dis}^\circ$
$H_2(g) \rightarrow 2H(g)$	104.2	$Br_2(g) \rightarrow 2Br(g)$	46.1
$N_2(g) \rightarrow 2N(g)$	226.0	$Br_2(l) \rightarrow 2Br(g)$	53.4*
$O_2(g) \rightarrow 2O(g)$	118.3	$I_2(g) \rightarrow 2I(g)$	36.1
$F_2(g) \rightarrow 2F(g)$	36.6	$I_2(s) \rightarrow 2I(g)$	51.0*
$Cl_2(g) \rightarrow 2Cl(g)$	58.0		

\* These values for bromine and iodine include heat of vaporization for these elements. (which are not mainly in gaseous state at 25°C).

SOURCE: Taken from *Circular of the National Bureau of Standards 500*, Washington, 1952, except for the value for nitrogen, which is taken from K. B. Harvey and G. B. Porter, *Introduction to Physical Inorganic Chemistry*, Addison-Wesley Publ. Co., Reading, Mass., 1963.

The energies necessary for many such dissociation reactions have been measured. Examples are listed in Table 16-3. For diatomic molecules, the dissociation energy,  $\Delta H_{dis}^\circ$ , can also be called the **bond energy**, the amount of energy per mole required to break the bond and produce two atoms.

Bond energies in compounds can be calculated by using values of the dissociation energies of elements together with the enthalpies of formation of the compounds. We can use data from Tables 16-1 and 16-3 to illustrate the method of calculation.

**PROBLEM 4** Calculate the bond energy of HCl.

*Solution* The enthalpy change of the reaction  $HCl \rightarrow H + Cl$  is equal to the bond energy of HCl. We can calculate the  $\Delta H_r^\circ$  for this reaction by choosing appropriate reactions and by using Hess's law.

Because we wish to begin with HCl, we shall write the first equation accordingly:

	$\Delta H^\circ$
from Table 16-1: $2HCl \rightarrow H_2 + Cl_2$	2(22.06) kcal/2 moles HCl
from Table 16-3: $H_2 \rightarrow 2H$	104.2 kcal/mole $H_2$
from Table 16-3: $Cl_2 \rightarrow 2Cl$	58.0 kcal/mole $Cl_2$
addition yields: $2HCl \rightarrow 2H + 2Cl$	206.3 kcal/2 moles HCl
or $HCl \rightarrow H + Cl$	103.2 kcal/mole HCl

The dissociation energy or bond energy of HCl is 103.2 kcal/mole.

**PROBLEM 5** Calculate the bond energy of a single N-H bond in  $NH_3$ .

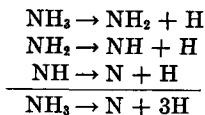
*Solution*

	$\Delta H^\circ$
from Table 16-1: $2NH_3 \rightarrow N_2 + 3H_2$	22.08 kcal/2 moles $NH_3$
from Table 16-3: $N_2 \rightarrow 2N$	226.0 kcal/mole $N_2$
from Table 16-3: $3H_2 \rightarrow 6H$	312.6 kcal/3 moles $H_2$
addition yields: $2NH_3 \rightarrow 2N + 6H$	560.7 kcal/2 moles $NH_3$
or $NH_3 \rightarrow N + 3H$	280.3 kcal/mole $NH_3$

In forming a molecule of  $NH_3$ , of course, three N-H bonds must be made. Because we want to calculate the bond energy of a single N-H bond, we divide by three.

for one mole of N-H bonds,  $\Delta H^\circ = 280.3/3 = 93.4$  kcal

The value of 93.4 kcal is thought of as the average bond energy per mole of N-H bonds in  $\text{NH}_3$ . In carrying out the decomposition of ammonia, one H would be lost at a time, and the process could be the result of three step-wise reactions:

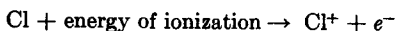
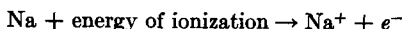


addition yields:

Actually, the individual enthalpy changes of the three reactions are not equal, but the average enthalpy change per step is 93.4 kcal.

## ENTHALPIES OF ELECTRON LOSS OR GAIN

**Enthalpies of Ionization.** The removal of an electron from a neutral atom requires energy:



The ionization energies of a number of elements were listed in Table 2-4 in terms of electron volts per atom. To calculate the ionization energy in kilocalories per mole of atoms (that is, the **enthalpy of ionization**,  $\Delta H_{\text{ion}}$ ) from the ionization energy per atom, the following conversion factors are needed:  $1 \text{ ev} = 1.602 \times 10^{-12} \text{ erg}$ ;  $1 \text{ kcal} = 4.184 \times 10^{10} \text{ erg}$ . We shall illustrate the method by calculating the enthalpy of ionization for sodium from the ionization energy of 5.14 ev per atom (Table 2-4):

$$\begin{aligned} \Delta H_{\text{ion}} &= \frac{5.14 \text{ ev}}{\text{atom}} \times \frac{1.602 \times 10^{-12} \text{ erg}}{1 \text{ ev}} \times \frac{1 \text{ kcal}}{4.184 \times 10^{10} \text{ erg}} \\ &\quad \times \frac{6.023 \times 10^{23} \text{ atoms}}{1 \text{ mole}} \\ &= \frac{5.14 \text{ ev}}{\text{atom}} \times 23.1 \frac{\text{kcal} \times \text{atom}}{\text{mole} \times \text{ev}} \\ &= 118 \text{ kcal/mole of sodium} \end{aligned}$$

The sign of  $\Delta H_{\text{ion}}$ , enthalpy of ionization, is positive, thus indicating that energy has been gained in the process. The factor 23.1 can be used to multiply any of the values in Table 2-4 to convert them from electron volts per atom to kilocalories per mole.<sup>1</sup>

**Enthalpies of Electron Affinity.** Another fundamental process involving atoms and electrons is the **electron affinity**, which is the energy released when an atom gains one electron. This process is obviously important in the case of those atoms which normally gain electrons in chemical reactions, that is, the nonmetals. But it is in-

<sup>1</sup> Calculations based on the data in Table 2-4 yield enthalpies of ionization at 0°K; values at 25°C are about 1.5 kcal higher.

interesting to note that energy is released even when an atom of a metal gains an electron, for example,  $\text{Na} + e^- \rightarrow \text{Na}^-$ . Of course, atoms of metals do not tend to gain electrons in reactions with nonmetals, because nonmetal atoms have greater electron affinities.

One measure of the electron affinity is the energy necessary to knock electrons off gaseous negative ions; the energy needed to separate an electron from the  $\text{Cl}^-$  ion must be equal in magnitude to the energy given up when the Cl atom gains one electron. Four examples of electron affinities per mole of ions are:

	$\Delta H_{ea}$
$\text{Cl}^- \rightarrow \text{Cl} + e^-$	87.1 kcal/mole $\text{Cl}^-$
$\text{Br}^- \rightarrow \text{Br} + e^-$	80.7 kcal/mole $\text{Br}^-$
$\text{Na}^- \rightarrow \text{Na} + e^-$	29 kcal/mole $\text{Na}^-$
$\text{K}^- \rightarrow \text{K} + e^-$	17 kcal/mole $\text{K}^-$

## ENTHALPIES OF IONIC CRYSTALS

Enthalpies of dissociation, as those which we considered previously for such molecular substances as  $\text{Cl}_2$ ,  $\text{HCl}$ , and  $\text{NH}_3$ , are of most interest in discussing covalent bond energies. For ionic compounds the bonding energy is best approached by considering a large number of ions in a crystal. The **crystal energy** (or lattice energy),  $\Delta H_{\text{stal}}$ , of a substance is the heat energy liberated per mole when widely separated gaseous ions come together to form a solid crystalline substance. The enthalpy change in this process is a measure of how strongly the ions are bound together.

The crystal energy of an ionic compound can be calculated theoretically on the basis of the charges, sizes, and arrangements of the ions in the solid, or it can be calculated on the basis of the measured energies of other reactions. The latter technique, called the Born-Haber method, was developed by the two eminent German scientists Max Born and Fritz Haber in 1919.

Crystal energies for a few compounds are given in Table 16-4. The direct measurement of the energy resulting from the coming together of gaseous ions or of the energy necessary to decompose a crystal into its gaseous ions is very difficult to measure experimentally. Values cited in reference books vary somewhat; the tabulation here shows ranges of probable values.

TABLE 16-4 *Probable ranges for crystal energies, kcal/mole*

substance	$\Delta H_{\text{stal}}$	substance	$\Delta H_{\text{sta}}$
LiF	-239 to -247	AgCl	-203 to -219
NaCl	-179 to -186	$\text{Li}_2\text{O}$	-690 to -700
KBr	-156 to -162	ZnS	-820 to -865
CsI	-135 to -144	HgS	-775 to -855

The Born-Haber cycle. The negative signs applied to  $\Delta H_f$  and  $\Delta H_{ea}$  show that the process occurring in the cycle as drawn is the reverse of the process as defined in the list on this page.

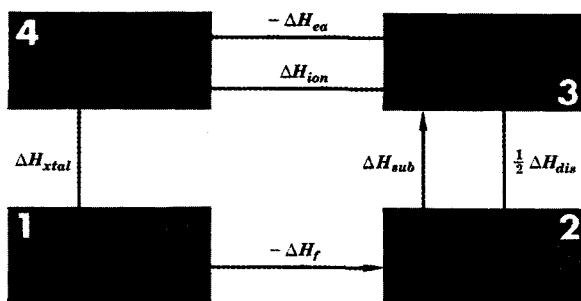


FIG. 16-1

## BORN-HABER CYCLE

To correlate many of the thermochemical reactions that we have been discussing, Born and Haber visualized a cyclical process involving a series of changes that could be analyzed using the law of Hess and the idea that in any closed cycle the net change in energy must be zero.

The Born-Haber cycle can be represented as in Fig. 16-1 for an alkali halide MX. To distinguish the various molar enthalpy changes,  $\Delta H$ , let us review the following definitions and symbols:<sup>1</sup>

change in enthalpy, as defined	symbol
formation, elements $\rightarrow$ solid compound	$\Delta H_f$
sublimation, solid metal $\rightarrow$ gaseous metal atoms	$\Delta H_{sub}$
dissociation, nonmetal $X_2 \rightarrow$ gaseous nonmetal atoms	$\Delta H_{dis}$
ionization, gaseous metal atom $M \rightarrow$ ion $M^+ + e^-$	$\Delta H_{ion}$
electron affinity, gaseous negative ion $X^- \rightarrow$ atom $X + e^-$	$\Delta H_{ea}$
crystal energy, gaseous ions $\rightarrow$ crystal	$\Delta H_{xtal}$

To illustrate the use of the Born-Haber cycle we can consider different processes, using Fig. 16-1 as a guide. First, suppose we start at state 1, one mole of the solid compound at 25°C and 1 atm, and pass successively through states 2, 3, 4, and back to state 1. Because the sum of all these enthalpy changes must be zero, we can write

$$-\Delta H_f + \Delta H_{sub} + \frac{1}{2}\Delta H_{dis} + \Delta H_{ion} - \Delta H_{ea} + \Delta H_{xtal} = 0$$

To assign the proper sign to each enthalpy quantity, we follow the code suggested by Fig. 16-1. Note that the minus signs in front of  $\Delta H_f$  and  $\Delta H_{ea}$  simply refer to the reverse of the defined processes, that is, decomposition rather than formation and electron gain rather than electron loss. Hence, when we look in tables for values of  $\Delta H_f$  and  $\Delta H_{ea}$  we change the signs given in the tables. For example,  $\Delta H_f$  for NaCl is  $-98.2$  kcal, hence  $-\Delta H_f$ , for the reverse process, is

<sup>1</sup> These terms and symbols are modeled after those used by K. B. Harvey and G. B. Porter in *Introduction to Physical Inorganic Chemistry*, Addison Wesley Publ. Co., Reading, Mass., 1962.

+98.2 kcal; or,  $\Delta H_{ea}$  for  $\text{Cl}^-$  is +87.1 kcal, so that  $-\Delta H_{ea}$ , for the reverse process, is -87.1 kcal.

Next, suppose we consider starting at state 1 and going to state 4 either directly ( $1 \rightarrow 4$ ) or indirectly ( $1 \rightarrow 2 \rightarrow 3 \rightarrow 4$ ). According to Hess's law, the enthalpy change by one path must equal that by any other, so that we can write

$$(1 \rightarrow 4) = (1 \rightarrow 2 \rightarrow 3 \rightarrow 4)$$

$$\text{or} \quad -\Delta H_{\text{xtal}} = -\Delta H_f + \Delta H_{\text{sub}} + \frac{1}{2}\Delta H_{\text{dis}} + \Delta H_{\text{ion}} - \Delta H_{ea}$$

We see that this form of the Born-Haber relationship is algebraically the same as the first form that we wrote.

At the time the Born-Haber cycle was developed, the most difficult quantity in the cycle to determine experimentally or to calculate theoretically was the electron affinity,  $\Delta H_{ea}$ . The equation was used in the form

$$\Delta H_{ea} = -\Delta H_f + \Delta H_{\text{sub}} + \frac{1}{2}\Delta H_{\text{dis}} + \Delta H_{\text{ion}} + \Delta H_{\text{xtal}}$$

to calculate electron affinities. In the 1930s, experimental determinations of  $\Delta H_{ea}$  began to be made, and these were found to be in fairly good agreement with the previously calculated values. Today the Born-Haber cycle is used to calculate thermochemical quantities not previously measured, especially crystal energies,  $\Delta H_{\text{xtal}}$ . The approach has been standardized and proved valid by applying it to the alkali halides, a class of compounds studied intensively for many years. For most other types of compounds less data and less precise data are available, so that the correlations are not always successful.

In Table 16-5 are listed representative values of various enthalpy

TABLE 16-5 *Born-Haber data for alkali halides, kcal/mole*

		Li	Na	K	Rb	Cs
	$\Delta H_{\text{sub}} =$	37.1	26.0	21.5	20.5	18.8
	$\Delta H_{\text{ion}} =$	124.2*	118.4	100.0	96.3	89.7
F	$\Delta H_{ea} = 81.0^*$	$\Delta H_f = -146.3$	-136.0	-134.5	-131.3	-126.9
	$\frac{1}{2}\Delta H_{\text{dis}} = 18.3$	$\Delta H_{\text{xtal}} = -244.9$	-217.7	-193.3	-185.4	-172.7
Cl	$\Delta H_{ea} = 87.1$	$\Delta H_f = -97.7$	-98.2	-104.2	-102.9	-103.5
	$\frac{1}{2}\Delta H_{\text{dis}} = 29.0$	$\Delta H_{\text{xtal}} = -200.9$	-184.5	-167.6	-161.6	-153.9
Br	$\Delta H_{ea} = 80.7$	$\Delta H_f = -83.7$	-86.0	-93.7	-93.0	-94.3
	$\frac{1}{2}\Delta H_{\text{dis}} = 26.7^\dagger$	$\Delta H_{\text{xtal}} = -191.0$	-176.4	-161.2	-155.8	-148.8
I	$\Delta H_{ea} = 73.5$	$\Delta H_f = -64.8$	-68.8	-78.3	-78.5	-80.5
	$\frac{1}{2}\Delta H_{\text{dis}} = 25.5^\dagger$	$\Delta H_{\text{xtal}} = -178.1$	-165.2	-151.8	-147.3	-141.0

\* All values of  $\Delta H_{\text{ion}}$  and  $\Delta H_{ea}$  are for 0°K, that is, about 1.5 kcal less than the values at 25°C. These two differences cancel one another in the Born-Haber cycle calculations.

† Values of  $\Delta H_{\text{dis}}$  for bromine and iodine include heat of vaporization, because these elements are not gases at 25°C.

SOURCE: Numerical data reproduced by permission from J. Kleinberg, W. J. Arger-singer, and E. Griswold, *Inorganic Chemistry*, D. C. Heath and Co., Boston.

relations for the alkali halides. The values for the crystal energies,  $\Delta H_{xal}$ , have been adjusted to give constant values for  $\Delta H_{ea}$  for each halogen and to make each Born-Haber cycle have a net enthalpy change of zero. To illustrate, the value of  $\Delta H_{xal}$  to be used in the table was calculated as follows for rubidium iodide, RbI, after a value of  $\Delta H_{ea}$  had been chosen:

$$\Delta H_{xal} = \Delta H_f - \Delta H_{sub} - \frac{1}{2}\Delta H_{dis} - \Delta H_{ion} + \Delta H_{ea}$$

$$\Delta H_{xal} = -78.5 - 20.5 - 25.5 - 96.3 + 73.5$$

$$\Delta H_{xal} = -147.3 \text{ kcal/mole}$$

The values for  $\Delta H_{xal}$  calculated in this way agree fairly well with those determined by other methods.

The student should also study the relationships between Fig. 16-1 and the data in Table 16-5 to learn how to assign the proper sign to each enthalpy change on the basis of whether the changes are exothermic (−) or endothermic (+). In a complete cycle, the heat given up in exothermic changes equals that taken up in endothermic changes.

The success of the Born-Haber treatment is, of course, a check on the theory that all the important steps in the cyclical process have been considered. The concept that the net heat energy change of any cyclical process must be zero is based on one of the most fundamental of all scientific laws, the **first law of thermodynamics**. One statement of this law is: *Energy can be converted from one form to another, but it cannot be created or destroyed*. Another way of stating the first law is: It is not possible to construct a perpetual motion machine. The first law underlies the very idea of the Born-Haber cycle: if it were possible to go through the cycle in either direction and gain heat energy, this heat could be used to do work and the cycle could be kept going perpetually. This is accepted as impossible. The first law of thermodynamics is an expression of the law of conservation of energy.

**Enthalpies and Structures of Substances.** An analysis of the information summarized in Table 16-5 and the other tables in this chapter enables us to illustrate a number of important concepts of general application.

For the alkali halides we note the regular trend of increase in crystal energy as the sizes of the ions decrease. If we look in any column or row of Table 16-5 and consider one class of compound say the bromides, we see that the crystal energy increases as we go from large ions to small ions. This rule can be generalized to describe compounds other than the alkali halides. In Table 16-4 we note the very high crystal energies of the compounds with small doubly charged ions. For ionic compounds, the higher the charge density<sup>1</sup> of the ions, the greater the crystal energy.

<sup>1</sup> See mention of charge density in Chap. 17.

We can also speak of the crystal energy of an element. The enthalpy of sublimation gives us a measure of the crystal energy of solid metals. The regular trend noted in Table 16-5 of increase in  $\Delta H_{\text{sub}}$  from cesium to lithium shows that lithium has the highest crystal energy of the group IA or alkali elements. The values of  $\Delta H_{\text{sub}}$  for the alkali metals, however, are low compared with other metals. For example, iron, cobalt, and nickel have enthalpies of sublimation of the order of 100 kcal/mole. This difference in energies necessary to change the crystals to gases is in accordance with the differences in properties: the alkali metals are soft, easily cut or deformed, have low melting points; the iron family metals are hard and tough, with relatively high melting points.

Trends in  $\Delta H_f$  show the relative ease of decomposing compounds into their elements. For chlorides, bromides, and iodides, Table 16-5 reveals that the stability of the compounds increases as the metal changes from Li to Cs. But for the fluorides the reverse trend holds. Writing an expression relating  $\Delta H_f$  to the other quantities helps us analyze these contradictory trends:

$$\Delta H_f = \Delta H_{\text{xtal}} + (\Delta H_{\text{ion}} + \Delta H_{\text{sub}}) + (\frac{1}{2}\Delta H_{\text{dis}} - \Delta H_{\text{ea}})$$

In each horizontal row, the halogen is the same, so that the quantity  $(\frac{1}{2}\Delta H_{\text{dis}} - \Delta H_{\text{ea}})$  is constant. In the case of the fluorides, the decreases in crystal energies,  $\Delta H_{\text{xtal}}$ , are greater than for the quantities  $(\Delta H_{\text{ion}} + \Delta H_{\text{sub}})$ , so that  $\Delta H_f$  becomes less energetic from LiF to CsF.

The fact that the fluorides differ from the other halides in trends in  $\Delta H_f$  is but one example of the anomalous behavior of fluorides. There is an apparent generalization that we can make even here, though. Just as fluorine and fluorine compounds differ in unexpected ways from the other halogens and their compounds, so oxygen (and its compounds) differs from the other group VIA elements, and nitrogen (and its compounds) differs from the other group VA elements. The elements in period 2 and their compounds commonly differ from what would be expected on the basis of trends in behavior describing other elements in the various groups. The very small sizes of the atoms and ions of the period 2 elements and their relatively simple electronic structures may be responsible for their anomalous behavior.

## FREE ENERGY

### ENTHALPY, ENTROPY, AND FREE ENERGY

Differences in the heat contents or enthalpies of reactants and products have a great deal to do with the way in which reactions take place. Obviously they determine whether a reaction is exothermic or endothermic. But enthalpy changes alone do not determine whether a chemical reaction tends to take place to a great extent or not. Or stated another way, enthalpy changes alone do not determine the position of equilibrium in a chemical system.

In addition to a change in enthalpy, practically every physical or chemical change involves a change in the relative disorder of the atoms, molecules, or ions involved. As mentioned in Chap. 10, the disorder or randomness of a system is measured by the **entropy**,  $S$ , of the system. A few simple examples will serve to illustrate the concept of entropy further.

A quantity of gas confined in a 1-liter flask has a higher entropy (greater disorder) than the same quantity of gas confined in a 10-ml flask at the same temperature. (See Fig. 16-2.)

When a small bulb containing either a volatile liquid or gas is crushed, the molecules become more randomly separated in the larger container; the entropy of the substance increases, and its free energy decreases.

Sodium chloride in the form of its gaseous ions has a higher entropy than in the form of a solid crystal.

Liquid water at 0°C has a higher entropy than ice at the same temperature.

To imagine a completely ordered system, we can think of a perfect crystalline element or compound at the temperature of absolute zero; *such a system would have perfect order, hence its entropy would be zero*,<sup>1</sup> but at any other temperature there would be some amount of disorder due to thermal excitation. The entropy of a substance compared with its entropy in a perfectly crystalline form at absolute zero is called its *absolute entropy*. The absolute entropy is, of course, always positive, because there is some disorder in any actual substance.

It is possible to calculate absolute entropies for substances at some standard condition, say 25°C and 1 atm, but the chemist makes more use of relative entropy values or changes in entropy,  $\Delta S$ , during chemical reactions. It will be recalled that  $\Delta H$  is the change in enthalpy for a process taking place at constant temperature and pressure. In general, a part of this enthalpy change is involved in changing the relative disorder or entropy of the system, and a part is associated with the useful work. The maximum amount of useful work that can be done by any process at constant temperature and pressure is called the change in the **Gibbs free energy**,  $\Delta G$ , named in honor of one of the greatest American theoreticians of the nineteenth century, J. Willard Gibbs.

At constant temperature, the changes in enthalpy, free energy, and entropy for any process, physical or chemical, are related by the equation

$$\begin{array}{rclcl} \Delta H & = & \Delta G & + & T\Delta S \\ \text{change in} & & \text{change in} & & T [\text{change in}] \\ \text{enthalpy} & = & \text{free energy} & + & \text{entropy} \\ \text{change in} & = & \text{change in} & + & \text{change in fixed energy} \\ \text{total energy} & = & \text{useful energy} & + & \text{of organization} \end{array}$$



F.G. 16-2

<sup>1</sup> This is a statement of the third law of thermodynamics.



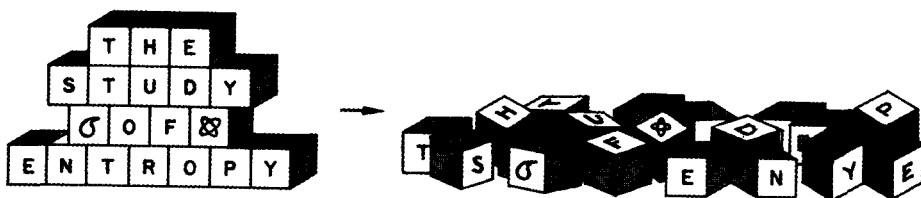


FIG. 16-3

An ordered system when disturbed tends to go to a disordered one; the entropy of the system increases.

We shall not have the occasion in this text to make many quantitative calculations of free energy and entropy changes, but there are some general principles with which we should be familiar. One of these is that, for any *spontaneous* change in an *isolated* system, there is an increase in the entropy of the system. Anyone who has to keep his own room straightened up can believe that the tendency toward disorder is a fundamental law of nature.

Closely associated with the concept of changes in entropy is the **second law of thermodynamics**. One statement of the second law is: *The total amount of entropy in nature is increasing*. Although we can pick out many natural processes that may involve increases in the degree of ordering (for example, the precipitation of salts in salt lakes or the growth of living organisms), other processes are taking place that decrease the order in nature (for example, the evaporation of water or the decay of organisms). The overall effects of the latter processes appear greater than of the former in the part of the universe that we observe.

Another way in which the second law is stated is: *In any spontaneous change the amount of free energy available decreases*. This is one way of saying that natural processes go downhill. (See Fig. 16-3.) A familiar example of the second law is that heat cannot pass from a colder to a hotter body without the action of some external agency.

Overall changes in nature or processes in which temperature changes occur are more complex than we wish to consider here. But in studying chemical reactions, the simpler case of processes at constant temperature is very important, and this case can be used to illustrate the way a change in entropy affects the course of a reaction. From the relation  $\Delta H = \Delta G + T\Delta S$ , we see that if  $\Delta H$  is specified, an increase in  $\Delta S$  must mean a decrease in  $\Delta G$ .

The change in free energy,  $\Delta G$ , rather than the change in enthalpy,  $\Delta H$ , determines whether a process tends to take place or not. A process at constant temperature can take place spontaneously only if  $G$  decreases, that is, if  $\Delta G$  is negative.

Let us consider the equation for the free energy in the form

$$\Delta G = \Delta H - T\Delta S$$

For most chemical reactions at room temperature  $T\Delta S$  is small compared with  $\Delta H$ ; therefore, the sign of  $\Delta G$  will usually be the same as

for  $\Delta H$ . That is, if a change is highly exothermic,  $\Delta H$  will have a large negative value, and  $\Delta G$  will be negative also. The process can take place spontaneously. A combustion reaction is an example of one such process that can proceed spontaneously.

On the other hand if  $\Delta H$  has a high positive value,  $\Delta G$  will probably be positive also, and the process will not take place spontaneously. The decomposition of a stable compound at room temperature is an example of such a nonspontaneous reaction. Table 16-6 gives the enthalpies of formation and the entropies for a number of elements and substances, and the corresponding free energies of formation. It will be noted that the sign of  $\Delta G$  is usually the same as for  $\Delta H$ .

For those cases which are only slightly exo- or endothermic, the change in entropy,  $\Delta S$ , may determine that the sign of  $\Delta G$  will differ

*Thermodynamic properties at 25°C and 1 atm*

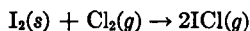
TABLE 16-6

element or compound	$\Delta H_f^\circ$ , kcal/mole	$\Delta G_f^\circ$ , kcal/mole	$S^\circ$ , kcal/(mole $\times$ deg)	log $K_f$
C(s)	0	0	0.00136	0
CH <sub>4</sub> (g)	-17.89	-12.14	0.0445	8.90
C <sub>2</sub> H <sub>2</sub> (g)	54.19	50.00	0.0480	-36.65
C <sub>2</sub> H <sub>4</sub> (g)	12.50	16.28	0.0524	-11.93
C <sub>2</sub> H <sub>6</sub> (g)	-20.24	-7.86	0.0548	5.76
CO(g)	-26.42	-32.81	0.0473	24.05
CO <sub>2</sub> (g)	-94.05	-94.26	0.0511	69.09
Cl <sub>2</sub> (g)	0	0	0.0533	0
H <sub>2</sub> (g)	0	0	0.0312	0
HCl(g)	-22.06	-22.77	0.0446	16.69
HN <sub>3</sub> (g)	70.3	78.5	0.0567	-57.54
H <sub>2</sub> O(l)	-68.32	-56.69	0.0167	41.55
H <sub>2</sub> O(g)	-57.80	-54.64	0.0451	40.05
Hg(l)	0	0	0.0185	0
Hg(g)	14.54	7.59	0.0418	-5.56
HgO(s)	-21.68	-13.99	0.0172	10.25
I <sub>2</sub> (s)	0	0	0.0279	0
I <sub>2</sub> (g)	14.88	4.63	0.0623	-3.39
ICl(g)	4.20	-1.32	0.0591	0.968
LiF(s)	-146.3	-139.6	0.0086	102.32
MgCl <sub>2</sub> (s)	-153.40	-141.57	0.0214	103.77
MgCl <sub>2</sub> (aq)	-190.46	-171.69	-0.0019	125.85
N <sub>2</sub> (g)	0	0	0.0458	0
NH <sub>3</sub> (g)	-11.04	-3.98	0.0460	2.91
NO <sub>2</sub> (g)	8.09	12.39	0.0575	-9.08
N <sub>2</sub> O <sub>4</sub> (g)	2.31	23.49	0.0727	-17.22
NaCl(s)	-98.23	-91.78	0.0173	67.28
NaCl(aq)	-97.30	-93.94	0.0276	68.86
O <sub>2</sub> (g)	0	0	0.0490	0
ZnCl <sub>2</sub> (s)	-99.40	-88.26	0.0259	64.69
ZnCl <sub>2</sub> (aq)	-116.48	-97.88	0.0009	71.75

NOTE: Aqueous solutions are ideal 1 molal.

SOURCE: Taken from *Circular of the National Bureau of Standards 500*, Washington, 1952.

from that of  $\Delta H$ . Such a case is the formation of iodine chloride,  $\text{ICl}$ . Although this is an endothermic compound, it has a favorable (that is, negative) free energy of formation at  $25^\circ$ , owing to the increase in entropy as  $\text{I}_2(s)$  and  $\text{Cl}_2(g)$  react to form  $\text{ICl}(g)$ :



From Table 16-6 we take data for the following calculations:

$$\Delta H_f^\circ = 2(4.20) - (0 + 0) = 8.40 \text{ kcal/2 moles ICl}(g)$$

$$\begin{aligned} T\Delta S &= T(\Sigma S^\circ \text{ products} - \Sigma S^\circ \text{ reactants}) \\ &= 298^\circ [2(0.0591) - (0.0279 + 0.0533)] \text{ kcal} \\ &= 298^\circ (0.1182 - 0.0812) \\ &= 11.03 \text{ kcal/2 moles ICl}(g) \end{aligned}$$

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 8.40 - 11.03 = -2.63 \text{ kcal/2 moles ICl}(g) \end{aligned}$$

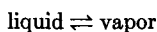
$$\Delta G^\circ = -1.32 \text{ kcal/mole ICl}(g)$$

The negative value of  $\Delta G^\circ$  indicates that  $\text{ICl}$  will form spontaneously at  $25^\circ\text{C}$ , even though it is an endothermic compound.

Finally, let us note that, as a system approaches equilibrium, its free energy  $G$  approaches a minimum. If a system is at equilibrium, it cannot spontaneously change to any other state with a lower energy; at equilibrium the free energy available for doing work is zero.

## FREE ENERGY AND EQUILIBRIUM

The free energy of a system is a state function, just as is the enthalpy, which is determined by the temperature and pressure. In a system at equilibrium, the tendency for a change to occur in one direction is just balanced by the tendency in the opposite direction. An example is a substance at its boiling point:



In this equilibrium system, the energy used in vaporizing is equal to the energy given up in condensing; the change in free energy,  $\Delta G$ , at equilibrium is zero.

Because for any process at constant temperature,

$$\Delta H = \Delta G + T\Delta S$$

in a process at equilibrium,

$$\Delta H = 0 + T\Delta S = T\Delta S$$

or

$$\Delta S = \frac{\Delta H}{T}$$

This equation relates the change in entropy for melting or boiling to the heat of fusion or vaporization, respectively. For many liquids, the value of  $\Delta S$  found by dividing the heat of vaporization by the absolute temperature at the boiling point is near the value of 21 cal/(mole  $\times$  deg K). This indicates that for many liquids there is about

the same increase in disorder (increase in entropy) when molecules closely packed in a liquid are vaporized into the random widely separated state characteristic of a gas.

## FREE ENERGY AND THE EQUILIBRIUM CONSTANT

*Relation of  $\Delta G^\circ$  to  $K_p$ .* The change in free energy of a chemical reaction is related to its equilibrium constant by the equation

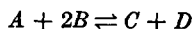
$$\Delta G^\circ = -RT \ln K_p$$

The term " $\ln K$ " stands for "the natural logarithm of  $K$ " and is equal to  $2.303 \log K$ . The term " $\log K$ " stands for "the logarithm of  $K$  to the base 10" (like those tabulated in the Appendix). The equation may be written

$$\Delta G^\circ = -RT 2.303 \log K_p$$

$R$  is the gas constant,  $1.99 \text{ cal}/(\text{mole} \times \text{deg})$ ;  $T$  is the absolute temperature; and  $K_p$  is the equilibrium constant.

Consider a gaseous reaction system at equilibrium:



For these equations as written, the chemist speaks of the reaction producing  $C$  and  $D$  as going to the right, or of the reaction producing  $A$  and  $B$  as going to the left. At equilibrium, of course, the rates of these reactions are equal, but there can be a great difference in the equilibrium concentrations of  $C$  and  $D$  as compared with  $A$  and  $B$ . Or, put another way, there can be a great difference in the tendency of the reaction going to the right to occur, as compared with that of the reaction going to the left.

The equilibrium constant for the reaction system is written as

$$K = \frac{[C] \times [D]}{[A] \times [B]^2} \quad \text{or} \quad K_p = \frac{p_C \times p_D}{p_A \times p_B^2}$$

depending on whether we use moles per liter or partial pressures to express concentrations. As we recall from Chap. 12, if the concentrations at equilibrium of  $C$  and  $D$  are large relative to  $A$  and  $B$ , then  $K$  (or  $K_p$ ) will have a large value; conversely, if  $A$  and  $B$  are large relative to  $C$  and  $D$ , the value of  $K$  (or  $K_p$ ) will be small.

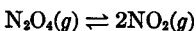
If  $K_p$  has any value larger than 1, say 100, its logarithm will be positive ( $\log 1 \times 10^2 = 2$ ). If  $K_p$  has a value less than 1, say 0.01, its logarithm will be negative ( $\log 1 \times 10^{-2} = -2$ ). The relationship between the size of  $K_p$  and the sign of  $\Delta G$  is apparent from the equation

$$\Delta G^\circ = -RT 2.303 \log K_p$$

If  $K_p$  is greater than 1,  $\log K_p$  is positive, and  $\Delta G$  is negative; if  $K_p$  is less than 1,  $\log K_p$  is negative and  $\Delta G$  is positive.

For a given equilibrium system, a negative value of  $\Delta G$  generally means that the reaction to the right as written tends to occur to a greater extent than that to the left. The more negative  $\Delta G$ , the greater is the relative tendency of the reaction to the right to occur. The converse is true for high positive values of  $\Delta G$ . If  $\Delta G$  is small numerically, say in the range of  $+3$  to  $-3$  kcal/mole, probably neither the reaction toward the right or left has an overwhelming tendency to occur; the equilibrium system will then consist of appreciable quantities of all possible reactants.

**CALCULATIONS.** The equilibrium decomposition of nitrogen tetroxide, described by F. H. Verhoek and F. Daniels in 1931, is an illustration of a reaction system in which neither the reaction toward the right or left tends to go to completion. For the system



at  $25^\circ$ , at a total pressure of 0.2118 atm,  $p_{\text{N}_2\text{O}_4} = 0.0950$  atm, and  $p_{\text{NO}_2} = 0.1168$  atm.

$$K_p = \frac{(p_{\text{NO}_2})^2}{p_{\text{N}_2\text{O}_4}} = \frac{(0.1168 \text{ atm})^2}{(0.0950 \text{ atm})} = 0.1436$$

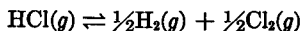
By determining  $K_p$  at several different pressures and extrapolating to zero pressure, the ideal value of  $K_p$  was calculated as 0.1426. The change in free energy is

$$\begin{aligned}\Delta G &= -RT \, 2.303 \log K_p \\ &= -(1.99)(298^\circ)(2.303)(-0.846) \\ &= +1160 \text{ cal} = 1.16 \text{ kcal/mole N}_2\text{O}_4\end{aligned}$$

The value of  $K_p$  is less than 1; therefore,  $\Delta G$  is positive. However, the positive value of  $\Delta G$  is rather small. This is to be expected, because the experimental data show that neither reaction has a great tendency to go to completion.

Perhaps the main use made of the relationship between  $\Delta G$  and  $K_p$  is the reverse of the type of calculation that we have just illustrated. From tabulated values of  $\Delta H$  and  $S$  the chemist can often calculate  $\Delta G$  for a system he is interested in, and from  $\Delta G$  calculate the equilibrium constant  $K_p$ . Knowing  $K_p$  and using methods like those illustrated in Chap. 12, the chemist can calculate concentrations of reactants at equilibrium under various conditions. Being able to predict the extent of reactions is of great importance in industrial chemical operations.

Let us consider an equilibrium system for which the value of  $\Delta G$  for the reaction to the right is fairly high and positive:



From Table 16-6 we see that  $\Delta G$  for the formation of HCl is  $-22.77$  kcal/mole; for the decomposition reaction (to the right as written above),  $\Delta G$  is  $+22.77$  kcal/mole. To calculate  $K_p$ ,

$$\Delta G = -RT \, 2.303 \log K_p$$

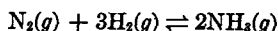
$$22,770 = -(1.99)(298^\circ)(2.303) \log K_p$$

$$\log K_p = -22,770/1366 = -16.67^* = \overline{17.33}$$

$$K_p = 2.1 \times 10^{-17}$$

This very small value of  $K_p$  shows that hardly any of the products  $\text{H}_2$  and  $\text{Cl}_2$  are present at equilibrium as compared with the amount of  $\text{HCl}$  present. This is in accordance with the prediction that we could have made. With a high positive value of  $\Delta G$ , we expect that a reaction has relatively little tendency to occur.

At  $25^\circ$ , for the following equilibrium system,



the value of  $\Delta G$  for the reaction to the right is negative:  $2(-3.98)$  kcal or  $-7960$  cal. This moderate decrease in free energy indicates that the reaction to the right has a fairly great tendency to occur and that  $K_p$  is large.

To calculate  $K_p$ ,

$$-7960 \text{ cal} = -(1.99)(298^\circ)(2.303) \log K_p$$

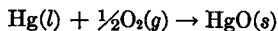
$$\log K_p = 7960/1366 = 5.83^\dagger$$

$$K_p = 6.8 \times 10^5$$

This large value, which agrees with our prediction, shows that, in the equilibrium as written, the reaction toward the right has a relatively great tendency to occur at  $25^\circ$ . As a practical matter, as we shall see in Chap. 23, the reaction is too slow at this temperature to produce ammonia efficiently. In fact, the reaction is so slow that the equilibrium constant at  $25^\circ$  cannot be determined directly but must be calculated, as above, from other data.

**Influence of Temperature on  $\Delta G$ .** A reaction to which we referred in Chap. 6 is at once a very simple reaction and an instructive one. If mercury is heated in oxygen (or air) just below its boiling point, it reacts with oxygen to form a red solid, mercury(II) oxide. But if the reactants are heated to a higher temperature, they do not react appreciably. In fact, at high temperature, mercury(II) oxide decomposes. Why should mercury and oxygen react only when heated, but if heated to too high a temperature not react? We can answer this question by considering the effect of changes in temperature on the free energy change of a reaction.

With the data in Table 16-6, we can calculate the free energy change,  $\Delta G$ , for the reaction



\* A value for  $\log K_p$  of  $-16.69$ , in accordance with Table 16-6, is obtained by use of more precise values for  $R$  and  $T$ .

† Note that the value of  $\log K_f$  of 2.91 in Table 16-6 is for the formation of 1 mole of ammonia.

under different conditions. Our aim is to evaluate  $\Delta G$  by estimating  $\Delta H$  and  $\Delta S$ .

We shall illustrate the calculation first at 25°C, for which we can calculate  $\Delta G^\circ$  precisely.

At 25°C,

$$\begin{aligned}\Delta H_r^\circ &= \Sigma \Delta H_f^\circ \text{ products} - \Sigma \Delta H_f^\circ \text{ reactants} \\ &= -21.68 - (0 + 0) = -21.68 \text{ kcal}\end{aligned}$$

$$\begin{aligned}T\Delta S^\circ &= T(\Sigma S^\circ \text{ products} - \Sigma S^\circ \text{ reactants}) \\ &= 298^\circ \{0.0172 - [0.0185 + \frac{1}{2}(0.0490)]\} \\ &= 298^\circ (0.0172 - 0.0430) = 298^\circ (-0.0258) \\ &= -7.69 \text{ kcal}\end{aligned}$$

and

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -21.68 \text{ kcal} - (-7.69 \text{ kcal}) \\ &= -13.99 \text{ kcal}\end{aligned}$$

The moderately high negative value of  $\Delta G^\circ$  shows that the reaction between mercury and oxygen has a considerable tendency to occur at 25°. However, we know from experience that mercury does not react with oxygen at room temperature. This means that, although the reaction can take place as far as free energy change is concerned, the activation energy for the reaction is so high that few if any molecules can react at 25°. The reaction is not occurring, for practical purposes.

Values for  $\Delta H$ ,  $\Delta G$ , and  $S$  differ at different temperatures. But we can use values like those in Table 16-6 for approximate calculations at various temperatures. One way of using the values is to assume that  $\Delta H$  and  $S$  remain about the same and calculate  $\Delta G$ . We shall use this approximate method for calculating  $\Delta G$  for the formation of HgO at two other temperatures.

At 300°C (573°K),

$$\Delta H \simeq -21.68 \simeq -22 \text{ kcal}$$

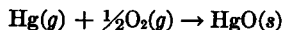
$$\begin{aligned}T\Delta S &\simeq 573^\circ(-0.0258) \\ &\simeq -15 \text{ kcal}\end{aligned}$$

and

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &\simeq -22 - (-15) = -7 \text{ kcal}\end{aligned}$$

The negative value of  $\Delta G$  indicates the formation of mercury(II) oxide will take place at about 300°C. This conclusion is consistent with experience, because one way of preparing mercury(II) oxide is to heat mercury in air, just below the boiling point of mercury (bp is 357°C). At 300°C the rate of the reaction is slow, but a long period of heating will yield some of the oxide.

At 500°C (773°K), which is 143° above the boiling point of mercury, we shall have to consider the mercury to be gaseous and calculate  $\Delta G$  for the reaction



$$\begin{aligned}\Delta H &= \Sigma \Delta H_f^\circ \text{ products} - \Sigma \Delta H_f^\circ \text{ reactants} \\ &\simeq -21.68 - (14.66 + 0) = -36.34 \\ &\simeq -36 \text{ kcal}\end{aligned}$$

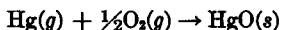
$$\begin{aligned}
 T\Delta S &= T (\Sigma S \text{ products} - \Sigma S \text{ reactants}) \\
 &\simeq 773^\circ \{0.0172 - [0.0418 + \tfrac{1}{2}(0.0490)]\} \\
 &\simeq 773^\circ (0.0172 - 0.0663) \\
 &\simeq -38 \text{ kcal/mole}
 \end{aligned}$$

and

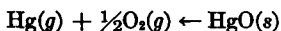
$$\begin{aligned}
 \Delta G &= \Delta H - T\Delta S \\
 &\simeq -36 - (-38) = +2 \text{ kcal/mole}
 \end{aligned}$$

Even though using  $\text{Hg}(g)$  as a reactant has caused  $\Delta H$  to become more negative,  $T\Delta S$  has changed to a greater extent with temperature, and  $\Delta G$  is therefore positive.

The positive value of  $\Delta G$  indicates that the reaction



has less tendency to take place at  $500^\circ\text{C}$  than the reaction



At  $500^\circ\text{C}$  mercury(II) oxide tends to decompose. If the oxide is heated in an open vessel and the oxygen allowed to escape, the decomposition goes to completion.

Let us conclude by repeating that these calculations are approximate, for the values of  $\Delta H$  and  $S$  do change with temperature, and over a range of hundreds of degrees these changes may be quite important.

## SUMMARY OF GENERAL PRINCIPLES

The example of the case of mercury(II) oxide serves to illustrate certain general principles which we have mentioned previously and which should be emphasized again.

1. *A negative value of  $\Delta G$  indicates that a reaction can take place spontaneously, but it does not tell us the reaction will take place.* The reaction rate may be practically zero if the activation energy for the reaction is high.

2. *At ordinary temperatures the value of  $\Delta H$  as a rule determines whether  $\Delta G$  is positive or negative.* An exothermic reaction with negative  $\Delta H$  will commonly have a negative  $\Delta G$  and take place spontaneously.

3. The entropy effect is usually small (a few calories per mole per degree), and  $T\Delta S$  at low temperatures is therefore small compared with  $\Delta H$  (which usually is of the order of kilocalories per mole). *Only for those cases in which  $\Delta H$  is small will the value of  $T\Delta S$  affect the sign of  $\Delta G$  at ordinary temperatures.*

4. *Any reaction that involves an increase in entropy will occur spontaneously at a high enough temperature.* If  $T$  is large enough, the product  $T\Delta S$  subtracted from  $\Delta H$  will result in a negative  $\Delta G$ , even if  $\Delta H$  is positive. Reactions that produce more disorder tend to be spontaneous at high temperature. The changes

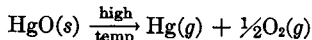
large molecules  $\rightarrow$  small molecules  $\rightarrow$  atoms

and

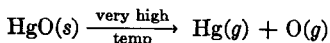
solids  $\rightarrow$  liquids  $\rightarrow$  gases



are favored at high temperature, because the entropy change is positive; as  $-T\Delta S$  becomes greater,  $\Delta G$  becomes more and more negative. The case of



illustrates this well. At a very high temperature the oxygen molecules would dissociate into atoms and increase the entropy even more:



5. All compounds decompose if the temperature is high enough. At extremely high temperatures even atoms decompose. In the interior of the sun nuclei and electrons are dissociated from one another.

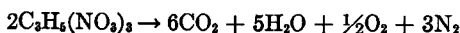
## CHAPTER REVIEW

### Terms

Standard enthalpy, absolute enthalpy, exo- and endothermic compounds, bond energy, dissociation energy, crystal energy, entropy, free energy;  $\Delta H_f$ ,  $\Delta H_r$ ,  $\Delta H_{\text{vap}}$ ,  $\Delta H_{\text{ion}}$ ,  $\Delta H_{\text{cat}}$ ,  $\Delta H_{\text{calal}}$ ,  $\Delta H_{\text{sub}}$ ,  $\Delta H_{\text{diss}}$ ,  $S$ ,  $\Delta S$ ,  $\Delta G$ ,  $\ln K$ ; Hess's law, law of Dulong and Petit, Born-Haber cycle; first, second, and third laws of thermodynamics;  $\Delta G = \Delta H - T\Delta S$ ;  $\Delta G = -RT \ln K_p$ .

### Exercises

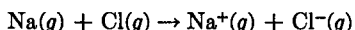
- Using symbols  $D$ ,  $E$ ,  $F$ , and  $G$  for elements, work out a hypothetical example illustrating Hess's law.
- Considering the data in Table 16-1, explain how one of the compounds—ammonia,  $\text{NH}_3$ , or hydrogen azide,  $\text{HN}_3$ —can decompose into its elements in a violent explosion. Calculate the change in heat per gram decomposed for each compound.
- Using the data in Table 16-1, determine the changes in enthalpy for the following reactions:
  - $2\text{H}_2\text{O}(l) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}_2(l)$
  - $2\text{C}_2\text{H}_6(g) + 7\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 6\text{H}_2\text{O}(l)$
  - $\text{CO}(g) + \text{H}_2\text{O}_2(l) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l)$
- List some measurements that would be needed and suggest some of the experimental difficulties in determining the absolute enthalpy of  $\text{HBr}(g)$  at  $25^\circ\text{C}$  and 1 atm.
- Assuming that the end products are carbon dioxide and water, calculate the approximate energy in kilocalories that the body receives during the oxidation of 10.0 g of glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ .
  - How much glucose would one have to oxidize to obtain enough heat energy to balance that lost by sitting in a tub of 4 ft<sup>3</sup> of water at  $60^\circ\text{F}$  till the water temperature rose to body temperature?
- Calculate the enthalpy change per gram for the decomposition of nitroglycerin, and state whether the reaction is probably spontaneous or not:



7. Would the  $\Delta H_f$  for methane at  $20^\circ\text{C}$  and 740 mm differ from its  $\Delta H_f^\circ$ ? Why?
8. On combustion, which yields the greater number of kilocalories per gram, ethane,  $\text{C}_2\text{H}_6$ , or acetylene,  $\text{C}_2\text{H}_2$ ?
9. If the measured heat of combustion of ammonia is  $-91.44$  kcal/mole, write the balanced equation for the reaction.
10. If 21.3 kcal is evolved when a mole of  $\text{SO}_3$  combines with a mole of  $\text{H}_2\text{O}$ , calculate  $\Delta H_f$  for anhydrous  $\text{H}_2\text{SO}_4$ .
11. Show how the enthalpy of formation of ethane,  $\text{C}_2\text{H}_6$ , could be calculated on the basis of experimental determinations of the heats of combustion of hydrogen, carbon, and ethane.
12. The heat of combustion of carbon disulfide,  $\text{CS}_2$ , is  $-257$  kcal/mole. Calculate the heat of formation of carbon disulfide.
13. Calculate the heat of decomposition of 1 g of  $\text{H}_2\text{O}_2$ .
14. The heat of combustion of methyl alcohol,  $\text{CH}_3\text{OH}$ , to yield  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is  $-5.33$  kcal/g.
  - a. Calculate  $\Delta H_f$  for  $\text{CH}_3\text{OH}$ .
  - b. Calculate  $\Delta H_f$  for  $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$ .
15. Calculate the heat value of methane,  $\text{CH}_4$ , in Btu per cubic foot. (See Table 1 of the Appendix.)
16. Is the reaction between  $\text{ZnCl}_2$  and  $\text{AgCN}$  to yield  $\text{AgCl}$  and  $\text{Zn(CN)}_2$  exo- or endothermic?
17. Calculate  $\Delta H_f^\circ$  for the following:
  - a.  $3\text{H}_2(g) + \text{N}_2(g) \rightarrow 2\text{NH}_3(g)$
  - b.  $\text{SO}_2(g) + \text{H}_2\text{O}_2(l) \rightarrow \text{SO}_3(g) + \text{H}_2\text{O}(l)$
  - c.  $3\text{NH}_3(g) + 2\text{O}_2(g) \rightarrow \text{HN}_3(g) + 4\text{H}_2\text{O}(g)$
  - d.  $2\text{CH}_4(g) + 3\text{Cl}_2(g) \rightarrow \text{C}_2\text{H}_2(g) + 6\text{HCl}(g)$
  - e.  $5\text{H}_2(g) + 2\text{NH}_4\text{NO}_3(s) \rightarrow 2\text{NH}_3(g) + \text{N}_2(g) + 6\text{H}_2\text{O}(l)$
  - f.  $2\text{HF}(g) + 2\text{Li}(s) \rightarrow 2\text{LiF}(s) + \text{H}_2(g)$
  - g.  $2\text{Fe} + 3\text{CO}_2 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{CO}$
  - h.  $3\text{Ca} + \text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe} + 3\text{CaO}$
  - i.  $\text{C} + \text{CaO} \rightarrow \text{CO} + \text{Ca}$
18. A metal with a specific heat of  $0.246$  cal/(g  $\times$  deg C) was found to react with oxygen in the ratio of 1.520 g metal per 1.000 g of oxygen. Calculate the oxidation number and the precise atomic weight of the metal.
19. By analysis of its oxide, a metal was found to have an equivalent weight of 29.67; its approximate specific heat was determined as  $0.056$  cal/(g  $\times$  deg C). What is the oxidation number and the precise atomic weight of the metal?
20. What do you think of the number of significant figures in column 4 of Table 16-2?
21. Consider Table 16-2. Assume that Dulong and Petit determined in their own laboratory the specific heat values tabulated in column 2 and

chose the atomic weights in column 3 from lists of values proposed by other workers. Which error in their laboratory work is the more serious, that with tellurium or cobalt?

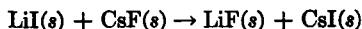
22. At the time of Dulong and Petit, possible acceptable values for the atomic weight of tellurium might have been 2.69, 4.03, or 8.06.
  - a. How did Dulong and Petit choose which of these atomic weights to use in their tabulation?
  - b. Assuming that tellurium oxide is 80.1 per cent tellurium, work out a possible oxidation number for tellurium and a formula for tellurium oxide that agree with the Dulong and Petit choice of an atomic weight for tellurium.
  - c. Repeat (b), using 8.06 for the atomic weight of tellurium.
  - d. Could one choose between 4.03 and 8.06 on the basis of possible tellurium oxide formulas alone; between 4.03 and 2.69?
23. One of the values that Dulong and Petit tabulated as the product of specific heat times atomic weight (see column 4, Table 16-2) is incorrect by several per cent. Find it and determine the percentage of error between the correct and incorrect values.
24. Calculate the bond energies in kilocalories per mole of bonds for  $\text{ClF}$ ,  $\text{ICl}$ , and  $\text{H}_2\text{O}$ .
25. a. If the sublimation energy for carbon,  $\text{C(s)} \rightarrow \text{C(g)}$ , is 172 kcal/mole, calculate the bond energies per mole of bonds for  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{CO}_2$ .  
b. What explanation can you suggest for the relative magnitudes of the bond energies in these three compounds?
26. Calculate the first ionization energies of fluorine and argon in ergs per mole and in kilocalories per mole.
27. Calculate the ionization energies in kilocalories necessary to form a mole of  $\text{Al}^{3+}$  ions; of  $\text{Ca}^{2+}$  ions.
28. Calculate the energy in kilocalories per mole for the following hypothetical reaction to yield separated ions:



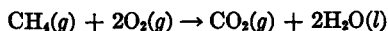
29. a. The first ionization energy of silver is 7.57 ev. Using appropriate data for silver chloride and chlorine from tables in this chapter, calculate the enthalpy of sublimation of silver.  
b. Express the probable error in the enthalpy of sublimation due to the approximate character of the least precise piece of data used.
30. Using the high and low values for the crystal energy of  $\text{LiF}$  in Table 16-4, calculate two values for the enthalpy of electron affinity for fluorine using a Born-Haber calculation and taking other data as needed from Table 16-5.
31. In general terms of atomic theory account for the following (see Tables 16-4 and 16-5):
  - a. The fact that  $\Delta H_{\text{stal}}$  for  $\text{LiF}$  is greater than for  $\text{CsI}$
  - b. The trend in the  $\Delta H_{\text{sub}}$  values for the alkali metals
  - c. The fact that  $\Delta H_{\text{stal}}$  for  $\text{ZnS}$  is greater than for  $\text{NaCl}$

- d. The fact that for the fluorides (in Table 16-5), going from Li to Cs, the values of  $\Delta H_f$  decrease and  $\Delta H_{\text{stal}}$  decrease; whereas, for the iodides, going from Li to Cs, the values of  $\Delta H_f$  increase and  $\Delta H_{\text{stal}}$  decrease

32. Calculate  $\Delta H_f$  for



33. Suppose the dissociation of a halogen molecule,  $\text{X}_2$ , were found not to be a single step to yield two X atoms, but rather a definite two-step process: first to yield an excited pair that later split into two atoms. How would this affect results obtained using the Born-Haber cycle, like those shown in Table 16-5?
34. Examine Table 16-6, and pick out a compound that has a positive  $\Delta H_f^\circ$  but a negative  $\Delta G_f^\circ$ . Calculate the bond energy of this compound.
35. The atoms of carbon in an ideal diamond are practically perfectly ordered. Is the absolute entropy of the carbon in this substance zero? Explain.
36. Which would have the greater entropy:
- A packaged deck of cards or the cards spread on a table?
  - An assembled automobile or the unassembled parts needed to make an automobile?
  - Carbon dioxide, water, and minerals or the stalk of corn that grows from them?
37. Explain in general terms the problem of determining the absolute entropy of nitrogen at STP.
38. Metal rod A is hot at one end and cold at the other; rod B has the same absolute heat content but has a uniform temperature. Which rod has the greater  $S$ ?
39. Consider the reaction



- According to the calculated  $\Delta G_r$ , does this reaction tend to occur spontaneously?
  - How do you account for the fact that  $\text{CH}_4$  and  $\text{O}_2$  can exist in contact indefinitely at room temperature without detectable reaction?
40. Calculate the change in entropy,  $\Delta S^\circ$ , for the reaction  $\text{S}(s) + \text{O}_2(g) \rightarrow \text{SO}_2(g)$ , given  $\Delta G_f^\circ = -71.79$  kcal/mole and the data in Table 16-1.
41. Using the data in Table 16-6, calculate  $\Delta S^\circ$  in two different ways for the reaction

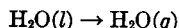


42. It has been determined that for the reaction



$\Delta H_f$  is  $-25.26$  kcal/mole and  $\Delta G_f$  is  $-29.44$  kcal/mole. Calculate  $\Delta H_f$ ,  $\Delta G_f$ , and the change in entropy for the formation of 1 mole of hydrogen peroxide gas.

43. From the data in Table 16-6, calculate the heat of vaporization per gram for



and compare your answer with the data in Table 7-5. Account for any discrepancy.

44. Using the data in Table 16-6, calculate the change in free energy,  $\Delta G^\circ$ , for the following reactions and state whether the reactions take place spontaneously or not:
- $2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$
  - $3\text{NH}_3(g) \rightarrow \text{HN}_3(g) + 4\text{H}_2(g)$
  - $2\text{HN}_3(g) \rightarrow \text{H}_2(g) + 3\text{N}_2(g)$
  - $\text{CH}_4(g) + 2\text{H}_2\text{O}(g) \rightarrow \text{CO}_2(g) + 4\text{H}_2(g)$
45. For each of the reactions in Exercise 44, calculate  $T\Delta S$  at  $25^\circ$ .
46. For each of the reactions in Exercise 44, calculate the equilibrium constant,  $K_p$ .
47. Trouton's rule states that for ideal liquids the molar heat of vaporization divided by the absolute bp is about 21 cal/(mole  $\times$  deg K). Using the data in Tables 7-2 and 7-4, check the validity of this rule for three substances.

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## MORE ABOUT

## STRUCTURE



At several places in the text we have discussed ways in which atoms join in various geometrical arrangements to form molecules or crystals. Particularly in Chaps. 4 and 7 we described the structures of some covalent and ionic substances. In this chapter we take up further aspects of structure, focusing attention first on some of the experimental evidence that physicists and chemists use to deduce the structures of molecules. We then summarize some of the important descriptions of structure as they apply to molecular, ionic, and metallic substances.

### SPECTROSCOPY AND MOLECULAR STRUCTURE

It is a fact that, when a substance is irradiated, it absorbs only certain wavelengths of radiation and allows others to pass through. (See Fig. 17-1.) The pattern of wavelengths that a substance absorbs is called its *absorption spectrum*. The study of such spectra is a part of the field of **spectroscopy**. According to spectroscopic theory, a given photon of radiation is absorbed by a molecule only when the photon can excite the molecule to some higher energy state.

As described in Chap. 3, the great success of the Bohr theory was that it accounted for the emission and absorption spectra of elements in terms of definite, *quantized* energy changes involving electron energy levels in atoms. Building on this theory, the absorption spectra of molecules are explained on the basis that each photon absorbed is used in exciting a molecule or a portion of a molecule in a definite way that requires a definite quantum of energy. A molecule absorbs a certain frequency of radiation (1) if some natural periodic movement of the molecule is in phase with that certain radiant frequency or (2) if the energy associated with a photon of the radiation is

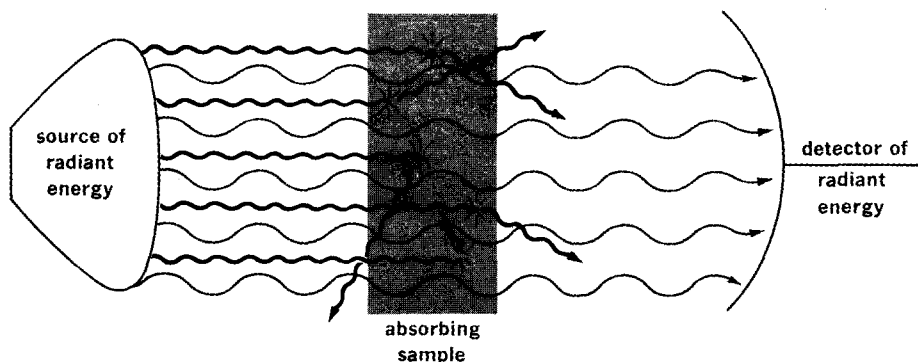


FIG. 17-1

Depending on the wavelength, radiant energy may be absorbed by a substance or may pass through unaffected. (Energy equivalent to that absorbed is radiated in random directions by the substance.)

sufficient to bring about a characteristic energy change of the molecule. Statement 1 uses the language of the wave theory of radiation, and statement 2 is made in terms of the particulate or photon theory. Both ways of looking at radiant energy, as a wave or as a stream of photons, are useful. We can even speak of a photon as having a wavelength corresponding to its energy as calculated by the equation  $E = h\nu = hc/\lambda$ .

As an analogy to the effect of radiant energy on a molecule, we can think of the effect of loud tones of music on a crystal goblet. When tones of appropriate wavelength are sounded, the goblet will efficiently absorb sound energy and vibrate with its own characteristic frequencies. The pattern of wavelengths absorbed by the goblet would be its sound absorption spectrum.

The arc emission spectra shown in Fig. 3-5 for several elements are *line spectra*, each line corresponding to a definite electron change in energy level or sublevel. The Fraunhofer lines shown in the spectrum of the sun illustrate absorption line spectra. The absorption spectra for molecular compounds are called *band spectra*, rather than line spectra, because the spectra as usually obtained consist of broad regions of absorption. Each region or band is found on close analysis to consist of many lines crowded closely together, so closely in many cases that only a spectrometer of great resolving power can separate them.

Even a simple molecule may have many more ways of absorbing energy than has an atom. Therefore, molecular absorption spectra are more complex than atomic absorption spectra. Consider a molecule of sulfur dioxide,  $\text{SO}_2$ . There are three nuclei with 32 electrons arranged such that some electrons are essentially held by a single atom, but other electrons are held jointly by two atoms. Each of the electrons can be excited to various higher atomic or molecular energy levels; an electron can even be separated from the molecule in an

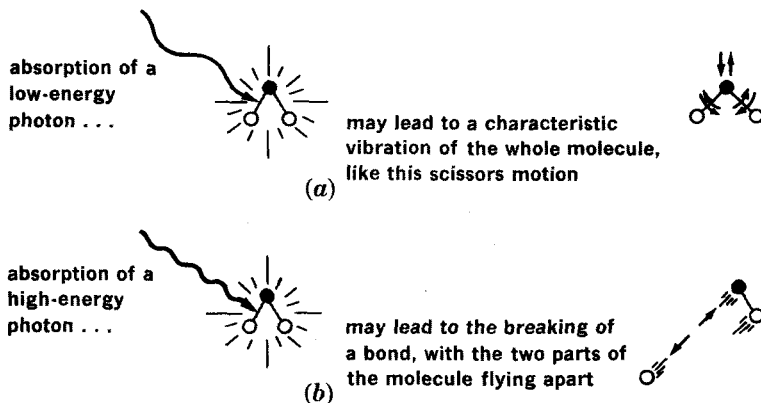


FIG. 17-2

A low-energy photon may cause a molecule to vibrate (a), whereas a photon with a sufficiently high energy can cause a molecule to decompose (b).

ionization reaction to form  $\text{SO}_2^+$ ; or the bonding electrons can be excited to such a degree that the bond is broken and the molecule is separated into two parts, SO and O (see Fig. 17-2).

*Effect of radiation on substances (see also Table 3-1)*

TABLE 17-1

approximate boundaries of various spectral regions*					
$\nu$ , $\text{sec}^{-1}$	$6 \times 10^{16}$	$2.5 \times 10^{16}$	$7.5 \times 10^{14}$	$4.3 \times 10^{14}$	$9 \times 10^{11} \text{ sec}^{-1}$
$\lambda$ , cm	$5 \times 10^{-7}$	$1.2 \times 10^{-6}$	$4 \times 10^{-5}$	$7 \times 10^{-5}$	$3.3 \times 10^{-3} \text{ cm}$
$\lambda$ , Å	$5 \times 10^1$	$1.2 \times 10^2$	$4 \times 10^3$	$7 \times 10^3$	$3.3 \times 10^6 \text{ Å}$
$E$ (ev per photon)	250	100	3.1	1.8	0.0037 ev per photon
$E$ (kcal per mole of photons)	5,800	2,300	72	41	0.085 kcal per mole

From the relationship  $E = h\nu = hc/\lambda$ , we can derive the following conversion factors: ( $E$  in ev) ( $\lambda$  in cm) =  $1.24 \times 10^{-4}$ ; ( $E$  in kcal) ( $\lambda$  in cm) =  $2.86 \times 10^{-3}$ ; and ( $E$  in ev) (23.1) = ( $E$  in kcal).

\* Different units are commonly used by spectroscopists who specialize in different fields of spectroscopy. For the infrared, wavelength is most often expressed in microns,  $\mu$ :  $1 \mu = 1 \times 10^{-4} \text{ cm}$ . In ultraviolet and visible work, both the millimicron,  $m\mu$ , and the angstrom are common units. In X-ray work, the angstrom unit is most often used.

The excitation of electrons in a molecule usually requires photons of energy lying in the visible or ultraviolet regions of the spectrum (see Table 17-1). There are other lower energy transitions that a



molecule can undergo that involve the bending and stretching of bonds in the molecule or the rotation of the molecule as a whole. These low-energy changes are brought about by photons in the infrared and microwave regions of the spectrum (see Fig. 17-2 and Table 17-1).

The study of the interaction of electromagnetic radiation with matter has been an inexhaustible mine of information during this century. The portions of the spectrum most useful in studying molecular structure are the ultraviolet, visible, and infrared regions, with some special applications of even lower frequency radiation.

## ULTRAVIOLET AND VISIBLE SPECTRA

A high-energy photon in the ultraviolet range may pack a wallop sufficient to knock an outer electron away from an atom or a molecule. In Table 2-4 we see that 10 ev is about average for the first ionization energies of the elements listed there. Using the Planck equation, we can calculate that 10 ev of energy is associated with a photon of radiation of wavelength  $1.2 \times 10^{-5}$  cm,<sup>1</sup> a wavelength within the ultraviolet range, as shown in Table 17-1.

Energies sufficient to ionize atoms (that is, first ionization energies) are sufficient to ionize molecules. Lower energies suffice to excite electrons from lower to higher energy levels and give rise to *electronic absorption spectra*. In molecules as in atoms, electronic excitations require energies in the range of 1.5 to 8.0 ev.

**Bond Energies.** If a photon has a high enough energy, it can cause a bond in a molecule to break. Such a gross chemical change as the decomposition of molecules is the main reason people must protect themselves from overexposure to high-energy radiation. The most serious damage by severe sunburn is due to the chemical reactions caused by the ultraviolet part of the sun's radiation. Molecules in the earth's upper atmosphere help protect us by absorbing much of the sun's ultraviolet radiation, but they do not absorb it all.

In Table 17-1 are listed the energies associated with radiations of different spectral ranges. The energy is expressed in two ways, in electron volts per individual photon and in kilocalories per mole ( $6.02 \times 10^{23}$ ) of photons. By studying the pattern of wavelengths absorbed by a substance, it is usually possible to determine the wavelength of the photon that has precisely the energy necessary to dissociate a bond. The energy of this photon is equal to the dissociation energy of the bond. By calculating the energy in kilocalories per mole

<sup>1</sup> As in Chap. 3, we would write  
 $E = h\nu = hc/\lambda$

$$\frac{10 \text{ ev}}{\text{photon}} = \left( \frac{6.63 \times 10^{-27} \text{ erg sec}}{\text{photon}} \right) \left( \frac{3 \times 10^{10} \text{ cm/sec}}{\lambda} \right) \left( \frac{1 \text{ ev}}{1.60 \times 10^{-12} \text{ erg}} \right)$$

$$\lambda = \frac{(6.63 \times 10^{-27}) (3 \times 10^{10})}{(10) (1.6 \times 10^{-12})} \text{ cm} = 1.2 \times 10^{-5} \text{ cm}$$

of photons (or per mole of molecules irradiated), we can relate bond energies or dissociation energies calculated from spectroscopic data to bond energies from thermochemical data (see Chap. 16).

A comparison of the energies of photons in kilocalories per mole with the molar dissociation energies listed in Table 16-3 shows that radiations in the visible and ultraviolet ranges are energetic enough to break certain molecular bonds. For example, molecular hydrogen,  $\text{H}_2$ , has a dissociation energy of 104 kcal/mole, corresponding to ultraviolet radiation of  $2.75 \times 10^{-5}$  cm wavelength. The chlorine molecule,  $\text{Cl}_2$ , with a dissociation energy of 58 kcal/mole, can have its bond broken by radiation of  $4.9 \times 10^{-5}$  cm wavelength. This radiation is in the blue-green region of the visible spectrum, as we can see by referring to Fig. 3-5.

Although spectroscopic analysis provides very precise calculations of bond energies, the interpretation of spectra is often difficult, for when a molecule is split into two parts, the parts themselves may be in excited states. The absorption line that corresponds precisely to the energy necessary to dissociate the molecule is surrounded in the spectrum by a great array of other lines, some lines at lower energies that are due to the excitation of electrons in the molecule, some lines at higher energies due to the breaking of the bond plus the excitation of one or both of the parts into which the molecule is split. The identification of the spectral line that corresponds to the simple bond-breaking energy can be made only after the consideration of many factors, often including the approximate determination of the bond energy by thermochemical methods. For example, iodine vapor,  $\text{I}_2$ , shows a continuous absorption of energy at wavelengths shorter than  $4.96 \times 10^{-5}$  cm (see Fig. 17-3). This indicates that with the shorter

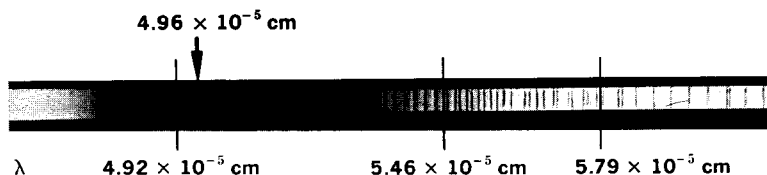


FIG. 17-3

The absorption spectrum of iodine vapor becomes continuous at  $4.96 \times 10^{-5}$  cm. The three lines marked in color are superimposed from the spectrum of mercury as known reference points. (Courtesy of Dr. W. H. Fletcher, The University of Tennessee.)

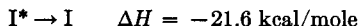
wavelengths the  $\text{I}_2$  molecule is dissociated into excited atoms with variable amounts of kinetic energy. However, even the energy associated with photons at  $4.96 \times 10^{-5}$  cm is equivalent to 57.7 kcal/mole, much more than the dissociation energy measured by thermochemical measurements of about 35 to 36 kcal/mole of iodine.

Analysis of the iodine spectrum reveals that the dissociation of an  $\text{I}_2$  molecule by a photon of  $4.96 \times 10^{-5}$  cm wavelength produces one

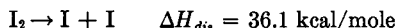
iodine atom in the unexcited (ground) state and one in an excited state:



The excited iodine atom emits energy equivalent to 21.6 kcal/mole when it changes into a ground state atom:



Addition of these two equations yields the energy of dissociation or enthalpy of dissociation of iodine into two atoms in the ground state:



Many other examples could be cited to show the difficulty of assigning specific frequencies to bond energies. Two decades ago the value of 63.5 kcal/mole was accepted as the dissociation energy of fluorine,  $\text{F}_2$ , on the basis of spectroscopic calculations. Recent thermochemical data indicate the value is much less than this, about 36 to 37 kcal. The value of 36.6 kcal/mole is cited today, the precise calculation being based on a reinterpretation of the spectrum of fluorine.

The nitrogen molecule,  $\text{N}_2$ , has an absorption spectrum that shows many lines in the ultraviolet. Possible dissociation energies calculated spectroscopically have included 170.18, 197.60, 225.96, and 272.0 kcal/mole. The value of 225.96 is most consistent with thermochemical data. The measurement of distances between spectral lines can be done with great precision, but less precise thermal data are often needed to help the spectroscopist choose which of the energy changes revealed in the spectrum is probably due to the breaking of the bond.

The dissociation energies of diatomic molecules used in Chap. 16, for example in the Born-Haber calculations, are based generally on spectroscopic calculations.

**Color and Chemical Constitution.** Color in substances is due to the selective absorption of part of the white light of the sun (or an artificial light) by molecules or atoms or ions. An object will appear to be blue, for instance, if it absorbs sufficient visible wavelengths in the green, yellow, orange, and red regions and reflects or transmits the radiation in the blue region. An object will also appear blue to the eye if it absorbs colors complementary to blue, in the orange region (near 5,900 Å), and transmits or reflects the remaining wavelengths of white light. If the absorption is in the yellow region (near 5,500 Å) the object will appear dark blue.

The absorption of visible wavelengths causes relatively low-energy reversible electronic transitions in molecules. In general, colored substances are thought to have some electrons that are rather loosely held, electrons easily excited.

The colors of substances are also discussed in connection with compounds of the transition elements in Chap. 19 and in connection with dyes in Chap. 26.

## INFRARED SPECTRA

Photons in the infrared radiation region are not energetic enough to cause electronic transitions, but they can cause the bending and stretching of bonds; that is, they can cause vibrations in molecules in which atoms change their relative positions. An atom has a large mass and is held in place in the molecule by a relatively weaker attractive force than is an electron; the atom, therefore, oscillates at lower frequencies. Electronic motions take place from  $10^{14}$  to  $10^{16}$  times per second, whereas atomic vibrations in molecules occur at the slower, but still respectable rate of  $10^{13}$  to  $10^{14}$  times per second (see Table 17-1).

The terms that the infrared spectroscopist has given to the various modes of molecular vibrations—twisting, wagging, rocking, scissoring, etc.—sound more like descriptions of a teen-age dance routine than like the staid language of science. Some of the possible motions in molecules are illustrated in Fig. 17-4.

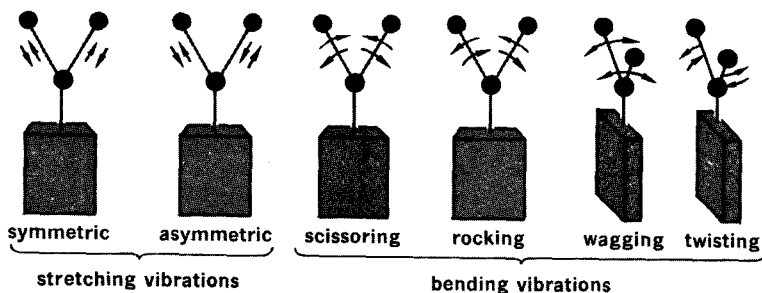


FIG. 17-4

Possible quantized motions, relative to the rest of a molecule, of two adjacent atoms. The motions alternate between those shown by the black arrows and those shown in color.

A definite quantum of energy is required to excite a certain molecular vibration; but in spite of this, the infrared spectrum of a molecule is a series of bands rather than lines. This behavior is due to the fact that molecules not only have **vibrational energy**, but also have **rotational energy**. A molecule that has a characteristic stretching frequency, for example, can absorb a photon that has more energy than is necessary to excite this stretch and use small quanta of the excess energy in increasing the rate of rotation. Or the molecule can absorb a photon that has a little less energy than its bond stretch requires but at the same time can convert quanta of its rotational energy into vibrational energy; it executes its characteristic stretch but rotates more slowly. The effect of this behavior is that the molecule absorbs photons of many frequencies close to its characteristic stretching frequency (rotational energy quanta are small compared to vibrational energy quanta). The close crowding of many absorption

## MORE ABOUT STRUCTURE

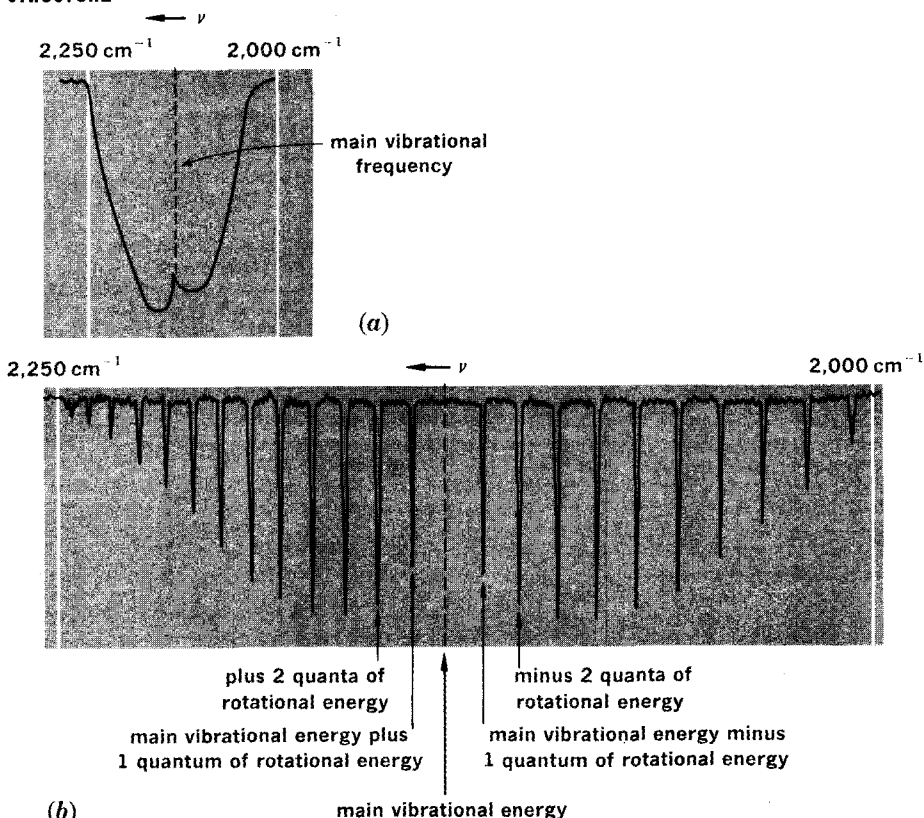


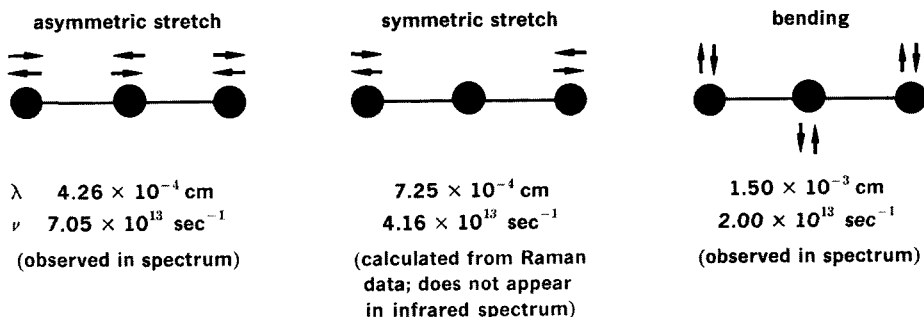
FIG. 17-5

Schematic representation of two methods of recording a spectral band: (a) represents a tracing (absorption) by a recording instrument such as that shown in Fig. 3-6. The wavelength absorbed due to a quantized vibration in the molecule can be read from the trace. However, to see the fine detail of this band, as is shown in (b), it must be spread out with a different type of spectrometer. Here the specific wavelengths absorbed due to both quantized vibrational and rotational energies are shown.

lines produces an *absorption band* (see Fig. 17-5) that shows maximum absorption at or near a true vibrational frequency.

Only those stretching and bending motions which change the dipole moment of a molecule give rise to absorption of infrared radiation. Consider the three possible fundamental vibrations of the  $\text{CO}_2$  molecule shown in Fig. 17-6. Although we might expect bands at wavelengths equivalent to each of these frequencies, only two of the bands appear. During the symmetric stretching of the  $\text{C}=\text{O}$  bonds, the dipole moment remains unchanged (zero), so that no absorption band is produced by this vibration. The frequency of this motion has been determined, however, by analysis of the electronic spectra and from Raman spectra (a branch of spectroscopy that we shall not discuss).

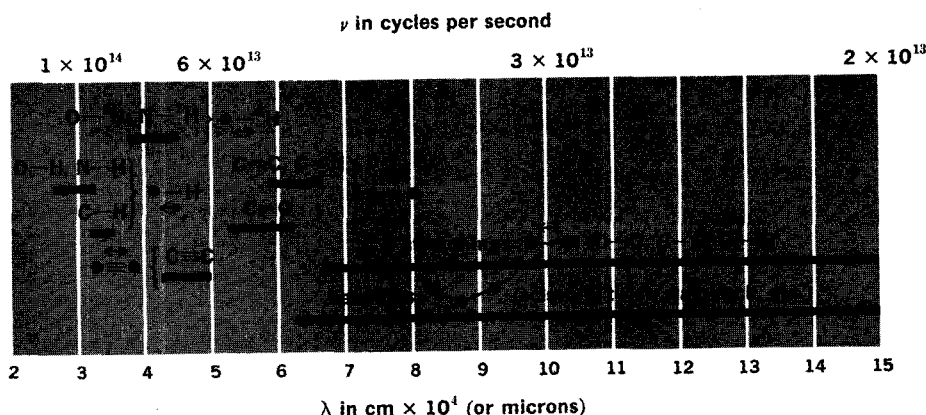
The wavelength and frequency regions associated with the stretch-



Three fundamental modes of vibration for the  $\text{CO}_2$  molecule, an example of a linear, symmetrical, nonpolar molecule.

FIG. 17-6

ing and bending vibrations of some common bonds in organic molecules are shown in Fig. 17-7. A few points can be emphasized in connection with these data. First, the data in the figure show that double bonds have higher stretching frequencies than single bonds between similar atoms. This indicates that double bonds (two pairs of shared electrons) are stronger than single bonds, so that more energy is required to excite double bonds. Second, the data show the effect on stretching frequencies of the masses of atoms. Bonds involving hydrogen have high frequencies, stretching about  $9 \times 10^{13}$  times a second as compared with  $2$  to  $5 \times 10^{13}$  times a second for the other single bonds described in Fig. 17-7. Note also that the substitution of the heavy hydrogen isotope,  $^2\text{H}$ , for the common  $^1\text{H}$  isotope lowers the frequency. The effect of a change in isotopic weight on stretching frequencies is shown in the case of other elements also,



Regions in the spectrum where lines for certain bonds are usually found. (Reproduced by permission from Koji Nakanishi, *Infrared Absorption Spectroscopy*, Nankodo Company Limited, Tokyo, 1962.)

FIG. 17-7

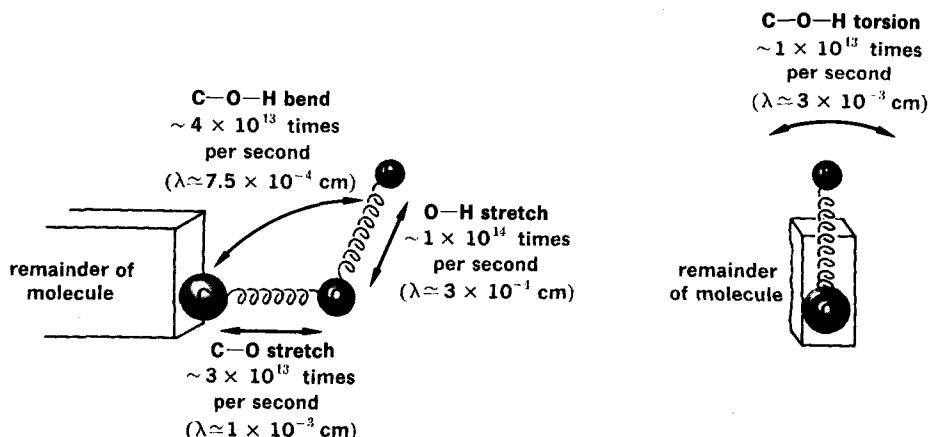


FIG. 17-8

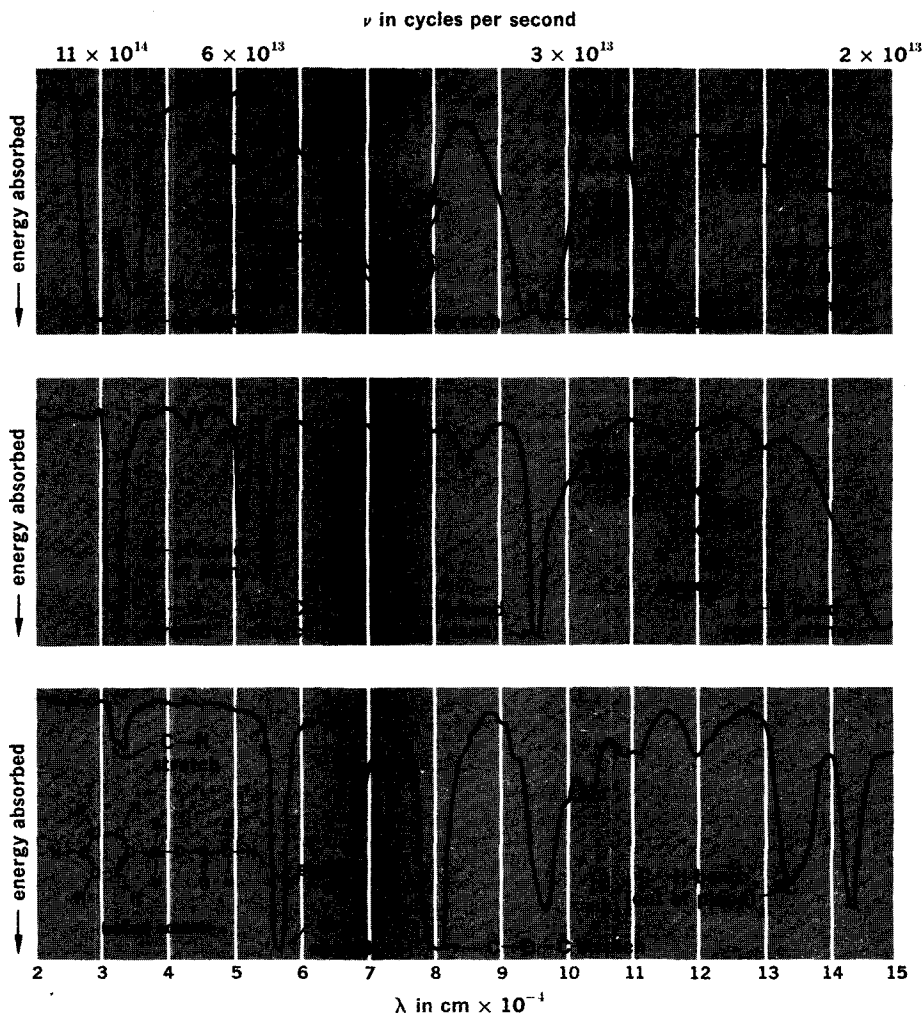
Vibrations of the  $\text{-C-O-H}$  (alcohol) group, explained in terms of a model in which spheres are connected by elastic springs. Approximate frequencies are given; precise values will differ depending on the nature of the remainder of the molecule. (Adapted by permission from Koji Nakanishi, *Infrared Absorption Spectroscopy*, Nankodo Company Limited, Tokyo, 1962.)

although the relative effect is less than for the change with hydrogen isotopes. The isotopes  $^{18}\text{O}$ ,  $^{15}\text{N}$ , and  $^{13}\text{C}$  were discovered by the spectroscopic detection of bonds involving them.

To help explain the vibrational frequencies measured by spectral data the physical chemist has made use of models of molecules in which small spheres (representing atoms) are attached to one another by steel springs (representing chemical bonds). Such a model is pictured in Fig. 17-8. The masses of the atoms, the geometry of a molecule, and the periods of the atomic vibrations can be related to one another and to the calculated stiffness of chemical bonds by use of the same equations of classical mechanics that apply to large vibrating masses or masses connected by stiff springs. In Fig. 17-8 the vibrational frequencies are shown for the alcohol group,  $\text{-C-O-H}$ , one of the important organic functional groups (see Chap. 27).

The infrared absorption spectrum of ethyl alcohol,  $\text{C}_2\text{H}_5\text{OH}$ , is shown in Fig. 17-9. The more complex a molecule, the more ways it will be able to absorb energy, and the more complicated its infrared absorption spectrum will be. Spectra for benzene,  $\text{C}_6\text{H}_6$ , and benzyl acetate,  $\text{C}_6\text{H}_5\text{CH}_2\text{OOCCH}_3$ , are also shown in Fig. 17-9. The structure of benzene is discussed in detail in Chap. 25.

From a study of infrared vibrational spectra the spectroscopist is able to calculate the relative strengths of bonds, their stiffness (resistance to bending), bond angles, and, for very small molecules, the overall geometry. Pure rotational spectra, in the far-infrared and microwave region, give especially important information on bond



The infrared absorption spectra of three organic compounds. (Alcohol spectrum courtesy of Prof. W. H. Fletcher, The University of Tennessee; benzene from Prof. R. Mecke, University of Freiburg [via the DMS System]; and benzyl acetate from R. W. Silverstein and G. C. Bassler, *J. Chem. Educ.*, **39**: 548 [1962].)

FIG. 17-9

distances and bond angles. In spite of bendings, stretchings, twistings, etc., average bond distances and bond angles are quite definite, being measured often to three or four significant figures.

The idea that the rotation of a molecule is quantized is a strange concept, but this conclusion is forced on us by the appearance of the sharp lines in the low-energy rotational region of the spectrum. The quantization of rotational energy means that a molecule does not rotate at just any rate, or a little faster or a little slower. For a given



## MORE ABOUT STRUCTURE

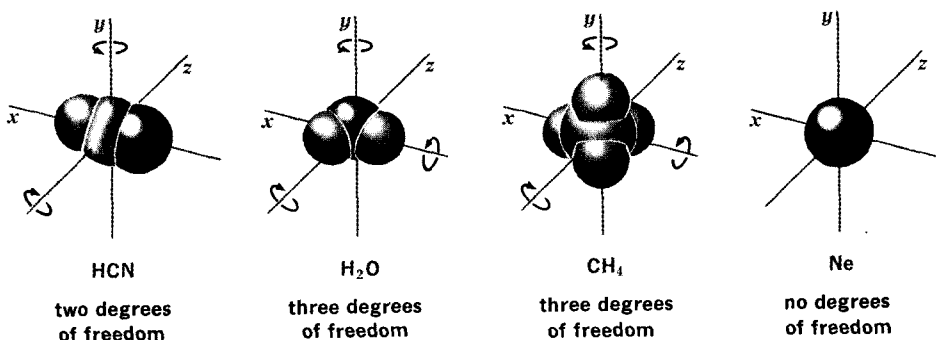


FIG. 17-10

Neither  $\text{CH}_4$  nor  $\text{Ne}$  have rotational spectral lines in the infrared; this shows they have no permanent dipole moments. By other means, however, it can be shown that the absorption of energy causes a  $\text{CH}_4$  molecule to rotate (change its orientation in space), whereas a  $\text{Ne}$  molecule does not absorb energy in rotating. If rotation about an axis changes its orientation, a molecule is said to have a rotational degree of freedom.  $\text{HCN}$  has only two rotational degrees of freedom because its rotation about the  $x$ -axis does not change its orientation.

molecule, a definite quantum of energy is required to raise it from one rotational energy level to the other.

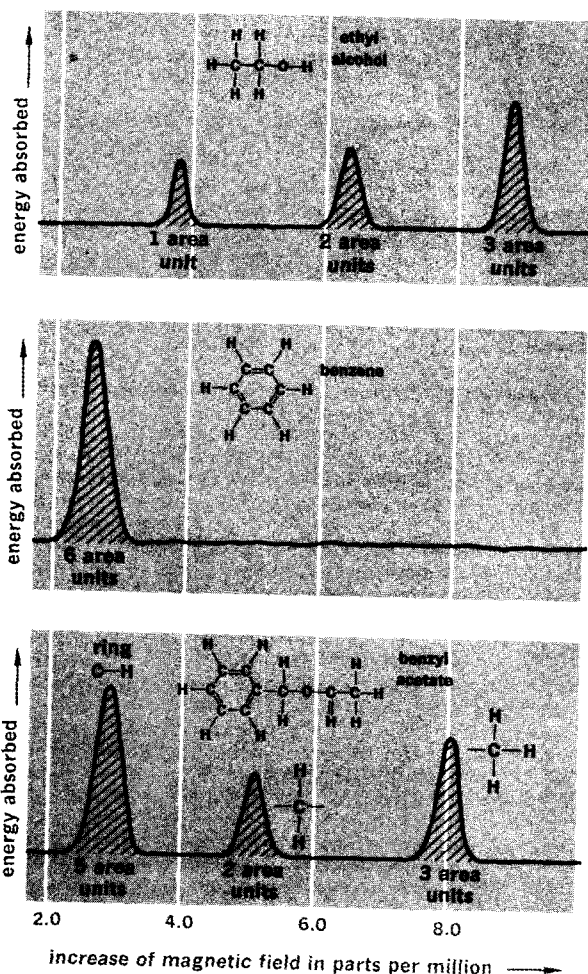
Molecules rotate with frequencies in the range of  $10^{11}$  times per second (see Table 17-1). Some types of rotational movement are diagrammed in Fig. 17-10. In order to exhibit a rotational spectrum, a molecule must have a permanent dipole moment; symmetrical molecules with zero dipole moments, such as  $\text{CH}_4$ ,  $\text{CCl}_4$ , or  $\text{CO}_2$ , have no observable spectral lines to indicate absorption of rotational energy.

Although much has been learned via infrared spectroscopy about the structures of complicated molecules, detailed descriptions of molecules containing more than a dozen atoms have yet to be achieved. The use of computers promises solutions to some of the problems encountered in these cases.

## NUCLEAR MAGNETIC RESONANCE SPECTRA

In 1945 a powerful new spectroscopic technique was added to the arsenal of the student of molecular structures. Professors Purcell, Torrey, and Pound of Harvard University and Bloch, Hansen, and Packard of Stanford University independently developed a device for detecting the very low energy interactions between certain atomic nuclei and magnetic fields, a phenomenon now called **nuclear magnetic resonance (NMR)**.

The phenomenon of NMR depends on the possession of a magnetic moment by the nuclei of certain atoms. Just as electrons behave as if they are spinning, so nuclear particles have spins. If the nuclear particles in a single nucleus do not have their spins paired, the nucleus



The low resolution hydrogen NMR spectra of three organic compounds.

FIG. 17-11

as a whole will have a resultant magnetic moment; such a nucleus tends to become aligned with an imposed magnetic field. The nucleus of the abundant isotope of hydrogen,  $^1\text{H}$ , has a magnetic moment, because it consists of but a single proton. The nucleus of a carbon-12 atom,  $^{12}_6\text{C}$ , has no resultant magnetic moment, because it consists of even numbers of protons and neutrons with paired spins.

In NMR spectroscopy, a sample of a compound is placed between the poles of a magnet powerful enough to align a portion of those nuclei which have magnetic moments. The sample then is irradiated with electromagnetic radiation, usually in the radiofrequency range of  $10^7$  to  $10^8 \text{ sec}^{-1}$ . A spinning nucleus aligned with the magnetic field can be flipped into a different alignment by absorbing a photon of precisely the proper energy. Different nuclei, or similar nuclei held in different electron environments, absorb photons of different wave-

length.<sup>1</sup> The pattern of radiofrequencies absorbed is the NMR absorption spectrum of the compound.

The most widely used NMR spectrometers measure the absorption of hydrogen nuclei,  $^1\text{H}$ , only. This permits a broad application, however, because hydrogen is present in more compounds, including almost all organic compounds, than any other element. By determining the placement of the hydrogen atoms in the structure of a molecule, the placement of other atoms can often be deduced.

Three hydrogen NMR spectra are shown in Fig. 17-11. The structures of the three compounds as drawn in Fig. 17-11 were well worked out by other techniques prior to the discovery of NMR, but they will serve to illustrate the almost unbelievable power of the NMR spectrometer to "see" a molecule and to sketch a report for the chemist in graphical form.

The hydrogen NMR spectrum of ethyl alcohol has three peaks, indicating that there are hydrogen atoms in this molecule held by three different kinds of bonds (or held in three different electron environments). The structure of ethyl alcohol as drawn shows three kinds of bonds: (1) an H-C bond involving a carbon atom on the end of the molecule, (2) an H-C bond to a carbon in the middle of the molecule, and (3) an H-O bond. The area under each peak in an NMR spectrum is proportional to the number of hydrogen atoms absorbing energy at that frequency. The relative areas under the peaks in the spectrum of ethyl alcohol show that in this molecule there are three hydrogen atoms held by the bond of type 1, two held by type 2, and one atom held by type 3.

The NMR spectrum of benzene,  $\text{C}_6\text{H}_6$ , is extremely interesting just because it is so simple. The single peak in the spectrum shows that each of the hydrogen atoms in the molecule is held by the same type of bond. This is strong evidence that the molecule is symmetrical, a property also indicated by other data (see "Benzene," Chap. 25).

The spectrum for benzyl acetate shows there are five hydrogen atoms held by one type of bond, two by another type, and three by a third. The structure as drawn agrees with this assignment.

The NMR spectra shown in Fig. 17-11 have the smooth, simple peaks characteristic of low-resolution spectra. With the precise measurements possible with a high-resolution spectrometer, some of these peaks can be shown to consist of several smaller peaks. The interpretations of high-resolution spectra reveal features of molecular structure that we shall not discuss.

## MISCELLANEOUS USES OF SPECTROSCOPY

*Analyses.* The great utility of spectroscopy in determining the

<sup>1</sup> In practice it is more difficult to vary the frequency of the radiation precisely than to vary the strength of the imposed magnetic field. NMR spectrometers commonly operate at a fixed radiofrequency and measure the changes in absorption of photons as the magnetic field is slowly varied.

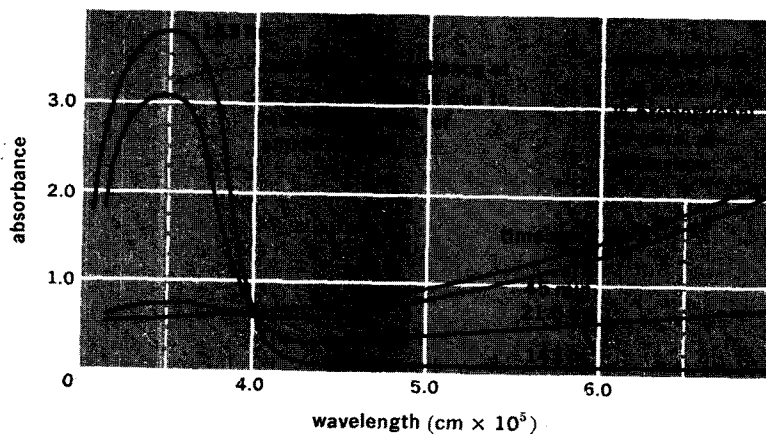


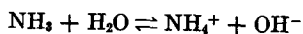
FIG. 17-12

Absorption spectra at different times of liquid ammonia solution of potassium during reaction  $K + NH_3 \rightarrow K^+ + NH_2^- + \frac{1}{2} H_2$ . As the reaction takes place, potassium is used and the absorbance due to it decreases (compare values in Table 12-2 and Fig. 12-2). As the reaction takes place, amide ion,  $NH_2^-$ , is produced, and the absorbance due to it increases.

structures of molecules and the strengths of chemical bonds is obvious, but there are many other important uses. Once the spectrum of a compound is known, it can be used to identify the compound. By precise measurement of spectral intensities, the percentage of a compound in a mixture can sometimes be determined. One of the reasons that spectroscopic detection is so useful is that usually only a tiny sample of the unknown is needed. As might be expected, law enforcement officials often rely on spectral analysis.

Spectroscopes are used in many industries to analyze raw materials and products. Spectroscopic standards have been established for colors of dyes and for brightness and colors of electric lights.

**Rates of Reactions.** In Chap. 12 it was mentioned that rates of reaction could be determined by following changes in concentration of reactants spectroscopically. In Fig. 17-12 are shown spectral curves of the type used to determine the data in Table 12-2. An interesting special use of NMR spectroscopy has been to show how very fast some reactions are. In Fig. 17-13 the NMR spectrum of very pure liquid ammonia,  $NH_3$ , is compared to the spectrum of ammonia containing a trace of water, possibly only 1 part of impurity in 10,000,000 parts of the mixture. The three peaks in the spectrum of pure ammonia indicate that the hydrogen atoms in an  $NH_3$  molecule maintain their positions in the molecule long enough to respond to the NMR radiant energy while they are attached to the nitrogen atom. The single peak in the other spectrum shows that a reaction such as



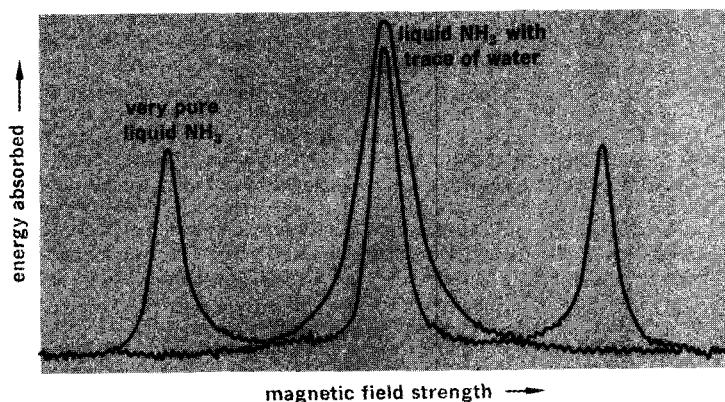
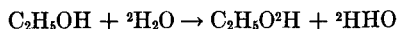


FIG. 17-13

NMR spectra of very pure ammonia and of ammonia containing a trace of water.

or simply a water-catalyzed exchange of hydrogen atoms between ammonia molecules is occurring so rapidly that the hydrogen atoms do not absorb energy as though they are bound to nitrogen atoms; rather they are moving freely from one nitrogen atom to another. It appears that in the presence of a trace of water a certain hydrogen atom is bound to a nitrogen in a  $\text{NH}_3$  molecule for less than 0.007 sec. The rates of rapid acid-base reactions have also been studied with NMR. The measurements of even faster reactions can be accomplished by spectroscopic techniques using higher-frequency radiation.

Because the NMR peak of the heavy hydrogen isotope,  $^2\text{H}$ , is in a different spectral region from the  $^1\text{H}$  peak, the heavy isotope is especially useful in studying the rates of hydrogen exchange reactions. If ethyl alcohol,  $\text{C}_2\text{H}_5\text{OH}$ , is put into heavy water,  $^2\text{H}_2\text{O}$ , the following reaction tends to occur:



As  $\text{C}_2\text{H}_5\text{O}^2\text{H}$  is formed, the NMR peak due to hydrogen held by the H-O bond in alcohol (see Fig. 17-11) disappears. The rate at which the H-O peak disappears is a measure of the rate at which  $^2\text{H}$  exchanges for  $^1\text{H}$ . It is also interesting to note that none of the hydrogen atoms attached to carbon atoms in ethyl alcohol exchanges with  $^2\text{H}$  atoms from the heavy water. The hydrogen attached to the O atom in ethyl alcohol is said to be *labile*, because it exchanges places readily with other labile hydrogen atoms (from the water).

## STRUCTURE AND PROPERTIES

As we have seen, the way in which atoms group themselves in many molecules and in crystals can be determined experimentally in several ways. After the chemist knows the geometry of a group, he concludes theoretically that, if one atom has four nearest neighboring

atoms, the first atom must be a partner in four bonds; if one atom has only two nearest neighbors, it must be a partner in two bonds. The atoms or groups attached to a central atom are called the *ligands* (Latin *ligare*, to bind) of the atom with which they are coordinated. The number of ligands is called the *ligancy* or *coordination number* of the central atom. The experimentally determined structures of many covalent molecules can be explained on the basis of a central atom with eight valence electrons. These eight electrons are often found to be paired so as to form four bonds that are directed out from the central atom toward the corners of a tetrahedron. For example, in the compound methane,  $\text{CH}_4$ , it is known that carbon is at the center of the molecule, that it has four nearest neighbors, and that the molecule as a whole has the shape of a regular tetrahedron. This means that the four bonds are directed out from the central carbon atom toward the hydrogen atoms that are at the corners of the tetrahedron (see Fig. 4-6).

Similarly, in the ammonium ion,  $\text{NH}_4^+$ , the nitrogen atom is at the center of the ion and the four hydrogen atoms are at the corners of a tetrahedron. In ammonia,  $\text{NH}_3$ , the nitrogen has three hydrogen neighbors. The three hydrogen atoms are at the three corners of a tetrahedron and the unshared pair of electrons on the N atom is directed toward the other corner.

In diamond (pure carbon) the carbon atoms are found at the corners of tetrahedra. And in silica,  $\text{SiO}_2$ , each silicon atom is at the center of a tetrahedron surrounded by four oxygen atoms (see Fig. 24-3).

The foregoing examples have been chosen to show how common the tetrahedral configuration is when an atom uses four pairs of electrons in combining with other atoms. The fact that tetrahedra are revealed so frequently by experimental means is strong evidence in favor of the theory that the outside energy level of an atom is very stable when it has eight electrons occupying four orbitals. However, four nearest neighbors is by no means a unique stable structure; for example, some atoms commonly have six ligands and so are at the center of octahedra; also planar structures are common, involving three or four ligands.

**Resonance.** With the development of methods for determining the shapes of molecules and the distances between atoms in molecules, it became increasingly apparent that in many cases diagrams that were based on completed shells of eight electrons were not satisfactory. A few examples will show how electron-dot formulas are not consistent with the determined properties of certain substances, such as ozone,  $\text{O}_3$ , sulfur dioxide,  $\text{SO}_2$ , and the carbonate ion,  $\text{CO}_3^{2-}$ .

The electron-dot formulas of these substances indicate that in each example there are some single bonds and some double bonds. It is well known that double bonds are shorter than single bonds. However, in each of the three cases discussed here, the molecules (or ion)

## MORE ABOUT STRUCTURE

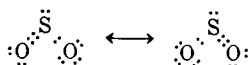
are symmetrical, and all the bonds are identical so far as can be determined. Because the dot formulas indicate incorrectly that there are bonds of different kinds, these formulas are not satisfactory:

unit	one possible electron dot formula	determined properties
ozone molecule	$\begin{array}{c} \ddot{\text{O}} \\ \vdots \\ :\ddot{\text{O}}::\ddot{\text{O}}: \end{array}$	both O-O bonds are same length (molecule is symmetrical)
sulfur dioxide molecule	$\begin{array}{c} \ddot{\text{S}} \\ \vdots \\ :\ddot{\text{O}}::\ddot{\text{O}}: \end{array}$	both S-O bonds are same length, 1.46 Å, a little shorter than a single bond but longer than a double bond (molecule is symmetrical)
carbonate ion	$\left( \begin{array}{c} \ddot{\text{O}} \quad \ddot{\text{O}} \\ \vdots \quad \vdots \\ :\ddot{\text{C}}::\ddot{\text{O}}: \\ \vdots \end{array} \right)^{2-}$	all C-O bonds are same length, and all bond angles are equal (ion is symmetrical)

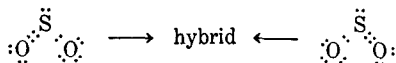
It is a striking fact that in the many cases in which the electron-dot formulas are not satisfactory, there is more than one logical way of writing a formula. Let us consider sulfur dioxide. In the dot formula above, we arbitrarily drew the double bond toward the left oxygen, but we could just as well have drawn it toward the right.

It is thought that, when a molecule (or ion) can be represented by two or more arbitrary structures that differ only in the arrangement of electrons, there is usually an intermediate structure that is more stable than any of the single arbitrary structures. Such an intermediate structure is said to be a **resonance hybrid**. The hybrid structure is more stable than any of the other "possible" structures.

Resonance is often indicated by drawing all the probable dot structures and indicating with a double-headed arrow that the actual structure is intermediate between these. Sulfur dioxide again serves as an example:



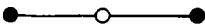
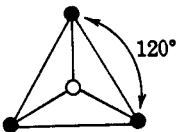
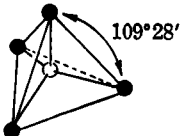
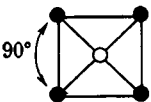
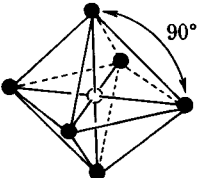
This representation is somewhat misleading, for it may suggest that the molecule has two forms and switches back and forth between them. A better representation is



This formula shows that there is one stable hybrid form, that this form is symmetrical, that the two S-O bonds are of the same length, and that the hybrid has an electronic arrangement that is intermediate between those of the two *resonance structures*.

The concept of resonance has been of great importance in explaining many details of structure, particularly the equivalence of certain bonds, symmetrical structures, and the stability of many molecules and ions.

*Hybrid orbital arrangements*

hybrids	number of orbitals	arrangement	examples
$sp$	2	linear 	$\text{HgCl}_2$ , $\text{Ag}(\text{NH}_3)_2^+$ , $\text{AgI}_2^-$
$sp^2$	3	equilateral triangular 	$\text{BCl}_3$ , $\text{NO}_3^-$ (?)
$sp^3$	4	tetrahedral 	$\text{CH}_4$ , $\text{CCl}_4$ , $\text{SiH}_4$ , $\text{NiCl}_4^{2-}$ , $\text{NH}_4^+$ , $\text{SO}_4^{2-}$ , $\text{NH}_3$ , $\text{H}_2\text{O}$
$dsp^2$	4	square planar 	$\text{Ni}(\text{CN})_4^{2-}$ , $\text{PtCl}_2(\text{NH}_3)_2$
$sp^3d^2$	6	octahedral 	$\text{SF}_6$ , $\text{Fe}(\text{CN})_6^{3-}$ , $\text{IF}_6$ , $\text{ICl}_4^-$

**Hybrid Orbitals.** In Chap. 4 examples were cited of the interaction of atomic orbitals to give molecular *hybrid orbitals*. The determination of the structures of a great variety of substances has shown that the concept of hybridization can be rather widely applied in relating the geometry of molecules and ions to the types of orbitals that are used in their bonds.

In Table 17-2 some common hybrid orbitals are listed along with their geometrical arrangements. The hybrid orbitals are named for the atomic orbitals originally associated with the central atom in the group. For example,  $sp^3$  refers to the four hybrid orbitals formed by the re-



arrangement and use of one  $s$  and three  $p$  orbitals from the central atom.

The coordination number (or number of ligands) of the central atom may equal the number of its hybrid orbitals, but this is not necessarily so. In the  $\text{NH}_3$  molecule there are four  $sp^3$  orbitals but only three ligands; one orbital consists of an unshared (nonbonding) pair of electrons. In the  $\text{H}_2\text{O}$  molecule the oxygen has two ligands and two unshared pairs of electrons involved in its four  $sp^3$  hybrid orbitals.<sup>1</sup>

When the number of ligands is less than the number of hybrid orbitals, the orbitals consisting of unshared (nonbonding) pairs take regular positions. The three octahedral structures for  $\text{SF}_6$ ,  $\text{IF}_5$ , and  $\text{ClF}^-$  are pictured in Fig. 21-2. Taking into consideration the nonbonding orbitals, each of the three is seen to have an octahedral geometry. Considering only the ligands,  $\text{IF}_5$  could be called a square pyramidal shape, and  $\text{ClF}^-$  a square planar shape.

**Properties of Covalent Substances.** There are a few nonmetallic elements, such as carbon and boron (see Chap. 24), that form crystals in which the atoms are tightly held in all directions by strong covalent bonds. In these elements there are no discrete small molecules held to one another by weak hydrogen bonds or van der Waals forces; indeed, a whole crystal can be considered to be one huge molecule. Such elements, and a few related compounds, are extremely hard, brittle substances. However, the great majority of covalent substances consist of collections of individual molecules. Atoms within these individual molecules are bonded together relatively tightly, and the individual molecules are attracted to one another relatively weakly.

In solid elements or compounds made up of covalent molecules, there are two general types of crystals. If the individual molecules are nonpolar or weakly polar, they pile together like marbles, taking up as little space as possible. If the individual molecules are polar, they arrange themselves in an efficient manner so that unlike charges are near one another and like charges are as far from one another as possible. A two-dimensional representation of the packing of polar molecules is shown in Fig. 6-8.

Nonpolar or weakly polar molecules form solids only at low temperatures (considerably lower than ionic substances do), because only van der Waals forces are operating to hold these molecules together. Such substances are the halogens, the hydrogen halides (except  $\text{HF}$ ),  $\text{CO}$  and  $\text{CO}_2$ , and many organic compounds, such as methane,  $\text{CH}_4$ , and other hydrocarbons (see Chap. 26).

Polar molecules are attracted to one another, not only by van der Waals forces, but also by the electrostatic attraction between their unlike charges. Such polar substances as  $\text{H}_2\text{O}$ ,  $\text{HF}$ , and  $\text{NH}_3$  have

<sup>1</sup> See page 137 for an alternative way of looking at the orbitals in the  $\text{H}_2\text{O}$  molecule.

higher melting and boiling points than similar but less polar compounds.

A single hydrogen atom in a polar molecule can be strongly attracted by another molecule; it bridges the gap between the two and forms a hydrogen bond. (See the discussion of  $\text{H}_2\text{O}$  and  $\text{HF}$  in Chap. 6 and 21, respectively.) From the graph in Fig. 21-7 showing the melting and boiling points of the hydrogen compounds of elements in groups IVA to VIIA, we see that certain polar molecules require higher temperatures to melt and boil, in spite of the fact that they are made up of small molecules when in the vapor phase. In the liquid and solid phases, molecules of these substances,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{HF}$ , are held together in larger aggregates by hydrogen bonds, which are considerably stronger than van der Waals forces. Compared with most of the other hydrogen compounds of V, VI, and VIIA elements, molecules of  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{HF}$  must have higher kinetic energies to overcome the strong forces that tend to hold them in fixed positions as solids or close together as liquids; that is, higher temperatures are required to cause melting or boiling.

The influence of molecular weight on melting and boiling points is quite straightforward so long as we compare molecules that are similar in structure. It is characteristic of a series of very similar molecular substances that the boiling and melting points increase as the molecular weights increase. This behavior is shown by all the compounds in Fig. 21-7 except for  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{HF}$ . Compare  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$  in this respect by referring to Table 21-1. Also compare the boiling points of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , etc., in Fig. 26-1.

## IONIC SUBSTANCES

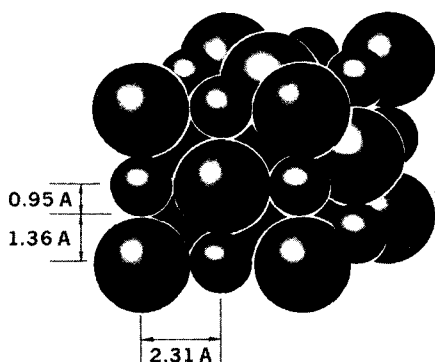
The principal difference between covalent and ionic compounds is that the former usually occur as discrete molecules, each containing a definite number of atoms, whereas the latter occur as crystals composed of an indefinitely large number of positive and negative

Crystals of calcium fluoride,  $\text{CaF}_2$ , showing cleavage along octahedral planes. These crystals, each about the size of a pecan, are considered single molecules. (Courtesy of Professor A. D. Melaven, The University of Tennessee.)

ions. Covalent bond forces, which are due to the overlap of bonding orbitals, are strong only at short range and depend on the directional character of the bonding orbitals. The attraction between ions, on the other hand, is electrostatic or coulombic; such forces act equally in all directions and attract unlike charges at relatively long range. Ionic compounds form what are called *infinite three-dimensional* crystals. An ordinary crystal of table salt is a three-dimensional collection of sodium,  $\text{Na}^+$ , and chloride,  $\text{Cl}^-$ , ions. (See also  $\text{CaF}_2$  in Fig. 17-14.) As described in Chap. 7, the distance between the nuclei of



FIG. 17-14



A diagram of a small portion of a sodium fluoride crystal.

FIG. 17-15

two adjacent ions can be determined by means of X-ray studies. In the ionic lattice of sodium fluoride the Na-F distance is 2.31 Å. Of this distance, 0.95 Å is assigned as the radius of the sodium ion, and 1.36 Å is the radius of the fluoride ion. (See Fig. 17-15.)

Simple monatomic ions vary in size from beryllium,  $\text{Be}^{2+}$ , with a radius of 0.31 Å, to one eight times as large, the antimonide ion,  $\text{Sb}^{3-}$ , with a radius of 2.45 Å. (Theoretically there are both larger and smaller ions, but such particles tend to form covalent bonds instead of existing as simple ions.)

Often an ion can substitute in an ionic lattice for another ion of the same charge and about the same size. Bromide ion,  $\text{Br}^-$ , has a radius of 1.95 Å and can often substitute for chloride,  $\text{Cl}^-$ , with a radius of 1.81 Å. However, an iodide ion,  $\text{I}^-$ , with a radius of 2.16 Å, can rarely if ever substitute in a crystal for a fluoride ion,  $\text{F}^-$ , with a radius of 1.36 Å. Figure 17-16 shows the layers of ions in four sodium halides.

A large ion or atom frequently does not substitute for a smaller ion or atom in a molecule or crystal. The larger particle is said to be kept out of the place of the smaller by **steric hindrance**; that is, the space available is just not large enough to accommodate the larger particle.

Three of the main influences on the patterns formed by positive and negative ions in crystalline solids are (1) the relative sizes of the two ions involved (called the *radius ratio*), (2) the charges on the ions, and (3) the ease with which the ions can be distorted or *polarized*, especially the negative ion.

Ions are considered to pack together as perfect spheres, just like marbles, unless the shape of one of the ions is distorted by a strong attraction to a neighboring ion of opposite charge. An isolated simple ion—for example, a large negative ion—should be spherically symmetrical with its charge evenly distributed; but if a positive ion with a highly concentrated charge (high charge density) comes very close to it, the negative ion may be pulled out of shape. As shown in Fig. 17-17, the distorted ion is not symmetrical, but is negative on one side (toward the positive ion) and positive on the other. The negative ion is said to be **polarized**, or to have an induced dipole moment.

Diagrams of four sodium halide crystals showing the difference in the relative sizes of the ions. As the anions increase in size, they approach each other more closely until in sodium iodide they practically touch (anion-anion contact).

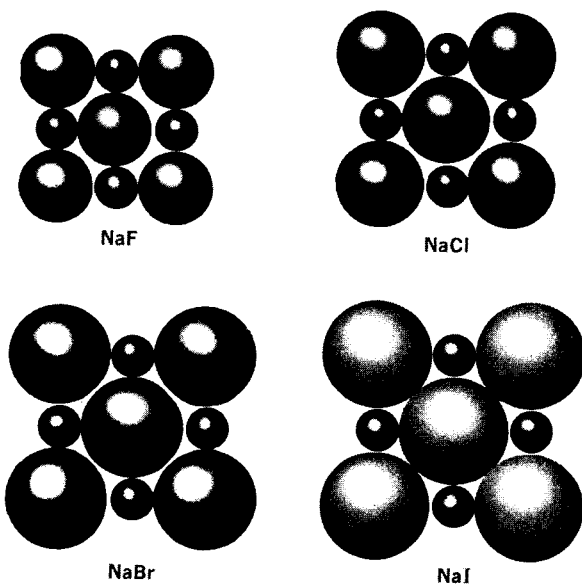


FIG. 17-16

Because of their greater size, negative ions tend to be polarized more easily than positive ones. The large  $\text{I}^-$  and  $\text{Br}^-$  ions are relatively easily distorted. A small, highly charged positive ion causes the polarization of negative ions.

Among effective polarizing agents are the ions  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Al}^{3+}$  (refer to Fig. 4-15 to estimate their relative sizes). In a compound made of large negative ions and small positive ions the polarization may be so marked that the bonds become somewhat covalent. Such *covalent-ionic* compounds include  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ , and  $\text{SnI}_4$ . (See Table 21-3.)

Schematic representation of the polarization of an ion.

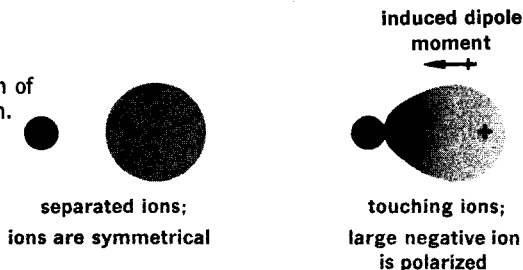


FIG. 17-17

## METALLIC SUBSTANCES

The simplest solids are those which contain just one kind of atom—for example, the metals. The atoms in metals are usually arranged in the most efficient possible fashion, just as we might pack oranges

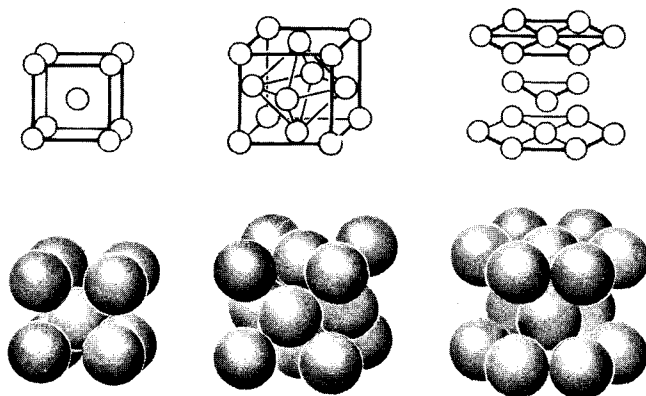


FIG. 17-18

The three common types of metal structures. From left to right: body-centered cubic, face-centered cubic, and hexagonal close-packed.

into a box. Three very common structures are drawn in Fig. 17-18.

In the body-centered cubic structure (Fig. 17-18), any atom (except those in the surface) has eight neighbors; in the face-centered cubic, any atom has twelve neighbors; in the hexagonal close-packed, any atom has twelve neighbors. The latter two are examples of the closest packing possible for identical spheres, whether one is considering atoms or cannon balls. Elements such as chromium, iron, tungsten, sodium, and potassium crystallize in the body-centered pattern. Face-centered lattices are formed by silver, aluminum, gold, copper, lead, and many other metals. Among the metals that form hexagonal close-packed lattices are cadmium, magnesium, and zinc.

The atoms in metals apparently are joined by a special metallic bond; it is certainly not an ionic bond; yet it is unlike a covalent bond. The most common metallic substances are elements, but there are many intermetallic compounds that have typical metallic properties.

Both metallic and certain nonmetallic elemental crystal structures, such as carbon, are similar to ionic structures in one important respect: the crystal is thought of as a single unit of indefinite size. Any single crystal of these solids, regardless of size, can be thought of as a molecule.

A recently developed instrument, the field ion microscope, has given the most striking direct experimental evidence for the symmetrical arrangement of atoms in metals. In this instrument there is a very highly charged, needle-pointed metal anode inside a tube similar to a television picture tube (Fig. 17-19). Stray atoms of helium gas strike atoms on the anode, are ionized, and are sent streaming toward the negatively charged screen end (or picture end) of the tube. The picture that appears on the screen (Fig. 17-20) has a pattern that is characteristic of the pattern in which atoms are crystallized in the metal anode.

Schematic representation of the field ion microscope. See also Fig. 17-20.

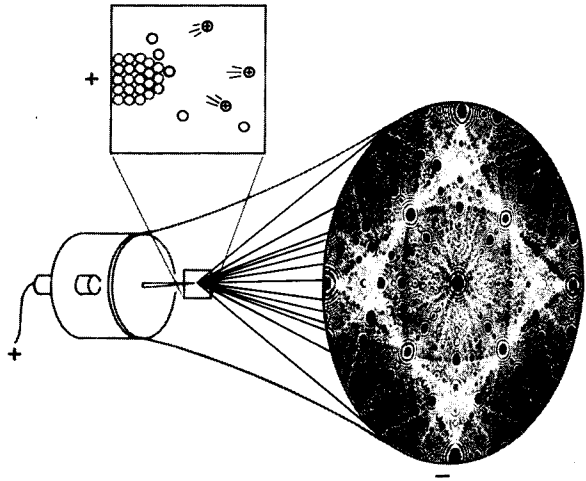


FIG. 17-19

A field ion microscope picture produced by using an anode made from a needle-pointed crystal of platinum. Each small luminous dot is an image of an individual platinum atom in the surface of the crystal. (Courtesy of Professor E. W. Mueller, The Pennsylvania State University.)

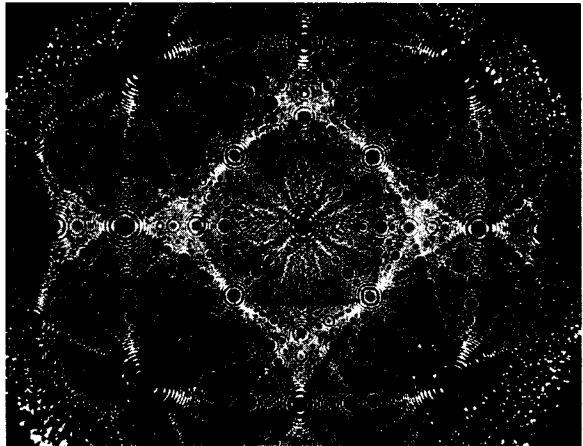


FIG. 17-20

**Properties of Metals.** Of the hundred-odd elements that are known, approximately 75 are classed as metals. Although these show a great diversity of properties, there are a few unifying characteristics, both chemical and physical, that serve to set them apart from the remaining nonmetallic elements. Remember that all metals do not exhibit metallic properties to the same degree; one metal may excel in certain characteristics, and another in other characteristics. In general, compounds do not possess these properties to a marked extent.

**PHYSICAL PROPERTIES.** The physical properties of most metals include the following characteristics.

1. A high degree of *electrical conductivity*.
2. A high degree of *thermal conductivity*.
3. A definite *luster*. The freshly broken, uncorroded surface of all metal elements except gold and copper is lustrous gray or silvery in color.
4. A *close-packed arrangement of atoms*. Typical structures include the three described in Fig. 17-18. As a result of this close packing, metals tend to have relatively high densities.
5. The ability to *change shape, without cracking, under strain*. Metals are malleable (they can be hammered into thin sheets) and ductile (they can be drawn into wires) in spite of the fact that their atoms hold strongly to one another.

**CHEMICAL PROPERTIES.** The chemical properties of most metals include:

1. A tendency to act as *electron donors* in reactions. Metallic ions are usually positive ions. This is related to the low ionization energy of metal atoms and to the fact that there are usually less than four electrons in their outside energy levels.
2. The formation of *basic oxides* for metals of low electronegativity.

**Metallic Bond.** The physical properties of the metals indicate that the valence bonds that hold the atoms in a metal together are not ionic, nor are they simply covalent in nature. These bonds are certainly not likely to be ordinary covalent bonds, because, although metal atoms commonly have only one to four outside electrons, they have 8 or 12 nearest neighbors. That is, there is less than one electron available per bond. According to the present view, a metal is composed of a rigid lattice of positive ions around which there is a sea or atmosphere of valence electrons. These valence electrons are restricted to certain energy levels, but they have sufficient freedom so that they are not shared continuously by the same two ions. When energy is applied, these electrons are easily transferred from atom to atom. This unusual bonding system, unique to the metals, is known as the **metallic bond**.

Unlike the ionic or covalent bond, the metallic bond provides for the strength and toughness of metals and at the same time permits deformation. Even though the positive ions occupy relatively stationary positions in the atmosphere of their electrons, they can glide over one another rather easily (Fig. 17-21); hence they do not give way in a complete fracture when the metal is hammered or rolled into thin sheets or pulled into a wire.

The high electrical conductivity of metals is attributed to the metallic bond. The fact that electrons are relayed (as electric current) through a crystal array of metal atoms with practically the speed of light indicates that some electrons are not held by individual atoms. Rather, the valence electrons in a metal belong to the solid as a whole. This helps explain high heat conductivity, also. If one end

On being distorted, a metal can still be strong because new metallic bonds are formed. On being distorted, an ionic crystal fractures. When oppositely charged ions slide close to one another, the strong repulsions force the crystal faces apart.

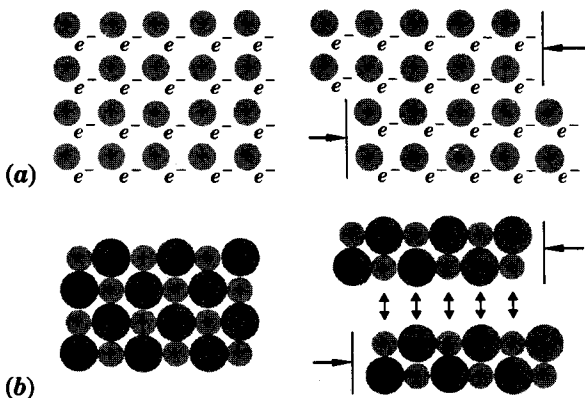


FIG. 17-21

of a piece of metal is heated, the electrons there move faster than electrons at the cold end. The rapid flow of heat in metals indicates that the energetic electrons at a hot spot move about rapidly and mingle with the rapidly moving, but less energetic, electrons in the cooler regions. This movement of valence electrons in metals and their interchange of energies is analogous to the random movement of molecules of a gas.

In conclusion, note that the metallic state is described primarily in terms of its physical properties. Elements are not the only materials that behave physically like metals. Two or more metallic elements can be mixed, or even combined chemically; the material thus formed is different from its components and has many of the properties of a simple metal. Such cases are taken up in Chap. 20 when *alloys* and kindred topics are discussed.

## SUMMARY OF STRUCTURE AND PROPERTIES

**Packing Together of Particles.** The individual particles that make up substances tend to arrange themselves in the most efficient way possible under any given set of conditions. In both molecules and crystals the particles naturally fall into patterns in which:

1. Particles attracted to one another are as close together as possible.
2. Particles repelled by one another are as far from one another as possible.
3. All the particles pack together in a symmetrical way so as to take up as little total space as possible.
4. The relative sizes (radius ratios) of bonded atoms may control the number of ligands. Very small central atoms tend to have low coordination numbers.

In describing crystal structures by means of diagrams, it is common



to represent them as geometrically perfect, both in arrangement and in numbers of particles involved. However, things are seldom perfect, and even crystals are no exception to this "law of nature." *Defect lattice structures* are common, which involve either missing atoms or ions (that is, holes in the crystal), or extra particles squeezed in here and there, or simply a disordered arrangement of the particles. In some samples of common salt it has been found that there are perhaps  $1 \times 10^{18}$  holes per mole (58.5 g). Although this seems to be a huge number of imperfections, it is only one hole per million ions.

Defect structures may have special electrical properties that are useful. Thus semiconductors, transistors, and insulators are made today from synthetic crystals that have carefully controlled defects.

**Bond Types and Structures.** Our discussion of chemical bonds has been in terms of three types: covalent, ionic, and metallic. In Chap. 4 we noted that often there was not a sharp division between covalent and ionic bonds, that bonds could be of intermediate character. In a like manner, there are bonds intermediate in character between metallic bonds and either covalent or ionic bonds.

In Fig. 17-22 a number of substances are given as having bond types of one of the three extreme types or as being of some intermediate bond type. Across the bottom of the triangle from right to left there is a gradual change, in a series of fluorides, from the highly ionic CsF (with a maximum difference in electronegativities) to the purely covalent  $F_2$ . The choice of  $IF_7$  as more covalent than  $SF_6$  might be questioned, because the electronegativity difference between iodine-fluorine is the same as for sulfur-fluorine, and the charge density of  $S^{6+}$  is greater than for  $I^{7+}$ .

Silicon fluoride,  $SiF_4$ , is a difficult compound to place, also. The electronegativity difference between silicon and fluorine of 2.2 units (see Table 4-3) would indicate that the bond is mainly ionic. Yet most chemists would consider  $SiF_4$  a covalent compound, because it exists as a gas at room temperature.<sup>1</sup> Owing to their tetrahedral symmetry, the  $SiF_4$  molecules are nonpolar, so that they are held to one another only by van der Waals forces. Because of its properties, silicon fluoride is classified as a covalent-ionic substance in spite of the fairly large difference in electronegativity between its elements.

Along the right side of the triangle in Fig. 17-22, going up from CsF to Li, the trend from ionic to metallic is illustrated by a series of sodium compounds. As the electronegativity difference decreases, the ionic character decreases. Compounds such as  $Na_3Sb$  and  $Na_3Bi$  are referred to as intermetallic compounds; some of their properties, such as heat and electrical conductivities, approach those of typical metals.

The trend from metallic to covalent bonding (down the left side of the triangle) is illustrated by elements from lithium to fluorine, listed roughly in order of increasing electronegativity from top to bottom.

Examples of the three simple types of bonding and of intermediate types of bonding. Adapted by permission from J. A. A. Ketelaar, *Chemical Constitution*, Elsevier Publishing Company, Amsterdam, 1953.

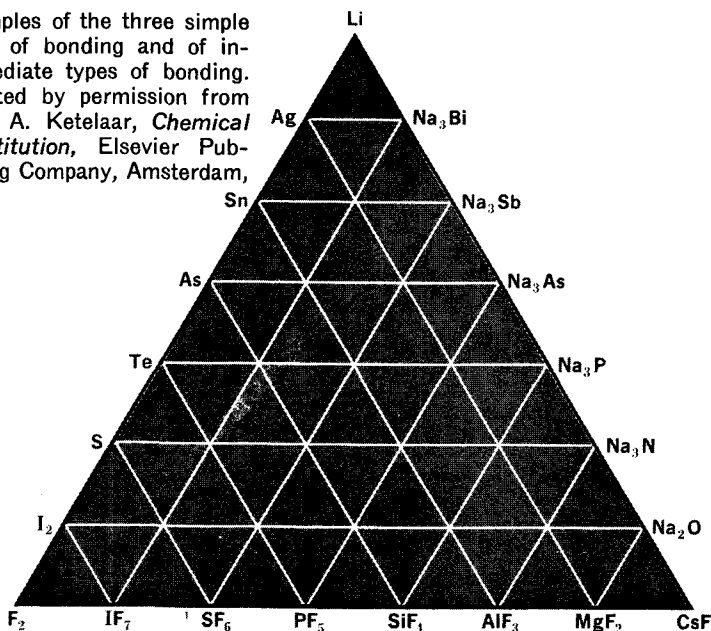


FIG. 17-22

Looking at the triangle in Fig. 17-22 in general terms, we see that an element with a high electronegativity is at the covalent corner (lower left), one with a low electronegativity is at the metallic corner (top), and elements with greatly different electronegativities form the compound at the ionic corner (lower right). In conclusion, let us repeat that most bonds are not of a pure type, but rather of an intermediate type. Compounds could be chosen for the middle of the triangle that would illustrate covalent-ionic-metallic bonding. The elements and compounds listed in Fig. 17-22 are simply suggested examples; others could be chosen that would be just as appropriate for many positions.

## CHAPTER REVIEW

### Terms

Spectroscopy, quantum of energy, line spectra, band spectra, infrared, ultraviolet, nuclear magnetic resonance (NMR), ligand, resonance, resonance hybrid, hybrid orbitals, steric hindrance, polarization, charge density, metallic bond;  $E = h\nu = hc/\lambda$

### Exercises

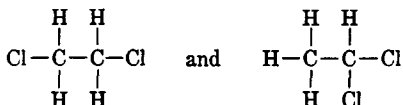
1. Account in general terms for the fact that a substance absorbs only certain wavelengths of radiant energy.

<sup>1</sup> Some general differences in properties of covalent versus ionic compounds were mentioned in Chap. 4. See also Table 21-3.

**MORE ABOUT  
STRUCTURE**

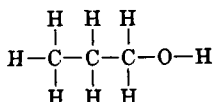
2. Which would require the higher energy photon:
  - a. The removal of an electron from  $\text{H}_2\text{O}$  or the exciting of the scissors motion in  $\text{H}_2\text{O}$ ?
  - b. The rotation of an  $\text{SO}_2$  molecule or the breaking of an S-O bond in  $\text{SO}_2$ ?
  - c. The excitation of the Cs atom to produce its blue emission line or excitation of the Na atom to produce its yellow emission line?
  - d. The stretching of a C-H bond in  $\text{C}_6\text{H}_6$  or the formation of the  $\text{C}_6\text{H}_6^+$  ion?
3. Show whether a photon of visible light is energetic enough to form a  $\text{K}^+$  ion from an atom.
4. Name the spectral region of a photon necessary to form a  $\text{Na}^+$  ion from an atom.
5. Name the spectral region of a photon energetic enough to cause the reaction  $\text{Li}^{2+} \rightarrow \text{Li}^{3+} + e^-$ ; to cause  $\text{B}^{3+} \rightarrow \text{B}^{4+} + e^-$ .
6. "In a molecule of carbon monoxide,  $\text{CO}$ , the C-to-O distance is 1.13 Å." Explain how this statement can be valid even though the bond is stretching with a certain frequency.
7. From the data in Table 2-4 we can calculate that radiation of wavelength  $1.62 \times 10^{-5}$  cm has the minimum energy necessary to knock one electron off a magnesium atom. Can magnesium absorb wavelengths of greater energy or less? Explain.
8. A low-wattage lamp is sometimes used to irradiate a drawer of surgical instruments to keep them sterile. Which would be preferable for this, an ultraviolet or infrared lamp?
9. A mixture of hydrogen and chlorine gases can be stored in a dry glass container in the dark for some time with no perceptible reaction. But if exposed to light, the two elements react violently. Explain.
10. It is well established that for the dissociation of a chemical bond a definite amount of energy is required and that this energy can be supplied by photons of precisely the proper wavelength. Yet it is often difficult to examine the absorption spectrum of a compound and determine the wavelength of the bond-breaking radiation. Explain.
11.
  - a. Consider the dissociation energy of fluorine. How is it possible to have confidence in a value like the presently accepted 36.6 kcal/mole, with three significant figures, when only a few years ago the value of 63.5 was being reported?
  - b. What additional data does the spectroscopist use to help him choose between 36.6 and 63.5 kcal/mole?
12. What wavelength radiation is necessary to dissociate gaseous bromine? Is this radiation in the visible spectral region?
13. Under a sodium vapor street light even colored objects usually appear black or various shades of yellowish gray. Explain.
14. Suppose a nitrogen molecule,  $\text{N}_2$ , strayed into the upper atmosphere. Show by calculation whether it could be dissociated by a cosmic ray. (See Table 3-1.)

15. *a.* Glass made with small amounts of cobalt compounds added is transparent but blue. Explain.
- b.* Optical glass is almost perfectly transparent. Does this mean it absorbs no radiation?
- c.* Suggest a reason for the fact that liquid samples for absorption studies in the ultraviolet are held in quartz containers, rather than in ordinary glass.
16. Two pieces of cotton cloth are dyed the same shade of blue, but with different dyes. On repeated exposure to sunlight one of the dyes fades much more than the other. Explain.
17. Consider two triatomic molecules, a linear one, like HCN, and an angular one, like H<sub>2</sub>O. Describe how their vibrations or rotations might differ.
18. Consider the scissors vibration of SO<sub>2</sub>. Although it is thought that photons of a definite energy are necessary to excite this vibration, the absorption spectrum of SO<sub>2</sub> shows not a sharp line but a band of absorption near the required energy. Explain.
19. The SO<sub>2</sub> molecule is angular, whereas the CO<sub>2</sub> molecule is linear. By means of a diagram explain how the symmetric stretching of the bonds in one could lead to a change in dipole moment, but not in the other.
20. Explain the following in general mechanical terms:
  - a.* The bonds that hydrogen forms have higher stretching frequencies generally than other single covalent bonds.
  - b.* The stretching frequencies of C-H bonds (say, in CH<sub>4</sub>) are higher if the carbon is <sup>12</sup>C than if it is <sup>13</sup>C.
  - c.* A C=C bond has a higher frequency than a C-C bond.
21. Is the stretching frequency of a certain type bond, like C-H, the same in different compounds? Illustrate your answer with examples. Explain in general mechanical terms why the stretching frequencies should behave in this fashion.
22. Consider the two compounds



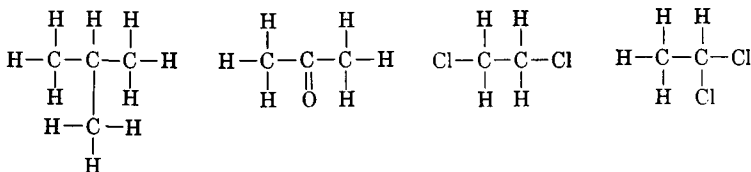
What sort of information would the infrared spectroscopist use to differentiate between samples of these compounds?

23. What feature of atomic structure gives rise to an NMR spectrum?
24. Consider the compound propyl alcohol:



- a.* How many different peaks would there be in the low-resolution NMR hydrogen spectrum of this compound?

- b. What would the relative areas under the peaks be?  
 c. Sketch an NMR curve for this compound and label the peaks.  
 d. Suppose that the isotope  $^2\text{H}$  were substituted for the H attached to the oxygen in propyl alcohol; answer (a), (b), and (c) with this modification.
25. a. When  $\text{CH}_3\text{OH}$  is exposed to heavy water, its NMR spectrum changes; but when  $\text{CH}_4$  is so exposed, its NMR spectrum does not. Explain.  
 b. When a small amount of ammonia is exposed to a large amount of heavy water, then separated and tested, it gives little or no  $^1\text{H}$  NMR spectrum at all. Explain.
26. Repeat Exercise 24a, b, and c for the compounds



27. Consider the structures of  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{NH}_4^+$  as described in this chapter. The measurement of what property (other than a spectrum) would indicate the overall geometry of each of these three?
28. For each of the following symmetrical species draw electron-dot formulas, including resonance forms where necessary. Assume each species is symmetrical and that bonds in each are identical:
- |                       |                    |                           |
|-----------------------|--------------------|---------------------------|
| a. $\text{SO}_3$      | c. $\text{NH}_3$   | e. $\text{H}_2\text{O}_2$ |
| b. $\text{SO}_4^{2-}$ | d. $\text{NO}_3^-$ | f. $\text{N}_2\text{O}_4$ |
29. The concept of resonance is often described as the tendency for a molecule "to resonate between two (or more) structures." Many chemists feel that such a statement suggests an erroneous idea. Explain.
30. What are some experimental and theoretical considerations that support the concept of resonance?
31. Molecules or ions that are made of atoms of two different elements often have symmetrical structures. If A stands for the central atom and B for those grouped around it, what shape would the following symmetrical species possibly have:  $\text{AB}_2$ ,  $\text{AB}_3$ ,  $\text{AB}_4$ ,  $\text{AB}_5$ ,  $\text{AB}_6$ , and  $\text{AB}_8$ ? What orbitals might be used in each case?
32. a. Write formulas for two binary compounds in which the central atom forms  $sp^3$  orbitals and in which the number of ligands the central atom has is four.  
 b. Repeat (a) for two binary compounds in which the number of ligands is less than four.  
 c. Would each of the four compounds that you chose in (a) and (b) have dipole moments?  
 d. Which of the four compounds would be likely to have low and which higher boiling points?
33. Consider a hypothetical covalent compound  $\text{AB}_2$ . What sort of experimental evidence would you seek to determine whether the bonds in it

result from the overlap of  $s$  and  $p$  orbitals,  $p$  and  $p$  orbitals, or hybridized orbitals. (Assume  $p^2$  to be nonhybridized bonds involving  $p_y$  and  $p_z$  orbitals.)

34. Give a couple of examples of a type of covalent compound in which the central atom utilizes  $sp^3$  bonds and has four ligands but in which the compound is polar.
35. Refute or justify the following statements:
  - a. "A perfect diamond can be thought of as a single molecule."
  - b. "A perfect snowflake can be thought of as a single molecule."
  - c. "A drop of pure liquid ammonia can be thought of as a single molecule."
  - d. "A perfect crystal of potassium bromide can be thought of as a single molecule."
36. a. Contrast the bonding in solid carbon (for example, diamond) and in solid chlorine. How do the differences in bonding help account for the differences in melting points?  
 b. Would it be preferable to phrase the preceding question as follows: "How do the differences in melting points (and other properties) indicate that there is a difference in the bonding in solid carbon and solid chlorine"? Give reasons for your answer.
37. Using the structure in Fig. 17-16 as a guide, calculate the radius of a positive ion that would just fit in the space remaining in an iodide crystal if the negative ions touch each other (anion-anion contact). Are there any alkali ions small enough to fit in the space? (Take data on ionic sizes from Tables 19-1 and 21-1.)
38. Cite evidence to show whether hydrogen bonding is more important in liquid  $NH_3$  or liquid  $H_2Se$ .
39. a. Which of the following isolated pairs of ions will involve the greatest degree of polarization:  $NaCl$ ,  $CsI$ ,  $CsF$ ,  $NaI$ , or  $KF$ ? Explain.  
 b.  $LiI$  has a crystal structure similar to  $NaCl$ . What sort of shape can we imagine for an  $I^-$  ion, in the interior of crystalline  $LiI$ , polarized somewhat by its neighbors?
40. If the strength of metallic bonds between atoms in metals is roughly proportional directly to the number of valence electrons per atom and inversely to the number of nearest neighbors, which of the following metals should be most malleable and which least: sodium, magnesium, or aluminum?
41. a. By means of a carefully drawn figure, show that, if a sphere were machined from a perfect crystal of metal having a body-centered cubic packing (Fig. 17-18), there would be different arrangements of atoms at various positions on the surface of the sphere.  
 b. Would the arrangement of atoms at some points on the sphere be hexagonal?  
 c. Repeat (a) and (b) for face-centered close packing.
42. Why do some atoms—for example, chlorine—form oxy-ions containing

## MORE ABOUT STRUCTURE

as many as four oxygen atoms, whereas other atoms—for example, iodine—form oxy-ions containing six?

43. How are electronegativity differences related to the types of structures formed by binary compounds?

## SUPPLEMENTARY READING

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## ELECTROCHEMISTRY;

## OXIDATION-REDUCTION

## EQUATIONS



For convenience, the field of electrochemistry may be subdivided into two classes: one dealing with chemical reactions that produce a current of electricity (the process occurring in a battery) and the other dealing with chemical reactions that are produced by a current of electricity (electrolysis). The first type of reaction is exothermic; the second is usually endothermic. There is nothing particularly mysterious or unique about electrochemical reactions. All are oxidation-reduction reactions in which the electrons being lost and gained by the reacting substances travel through conducting wires.

Before we discuss the two phases of electrochemistry, it will be necessary to consider briefly some of the units for measuring different characteristics of electric currents.

**Electrical Units. COULOMB.** The coulomb is defined as the quantity of electricity required to plate out 0.001118 g of silver from a solution of silver ions. Because a current of electricity is the flow of electrons through a conductor, a unit quantity of electricity is in reality an expression of the number of electrons that have passed through the circuit. On the basis of the charge of one electron, it is calculated that 96,500 coulombs corresponds to the passage of  $6.02 \times 10^{23}$  electrons. This quantity of electricity (96,500 coulombs) is called a **faraday**. It is the logical unit of quantity for the chemist, because it is the amount of electricity required to bring about the oxidation (or reduction) of one equivalent weight of any substance.<sup>1</sup>

<sup>1</sup> The coulomb is commonly defined in terms of the ampere. Based on this definition, the charge represented by a coulomb is equivalent to the charge of 0.001118 g of  $\text{Ag}^+$  ions. The definition of the coulomb is independent of the  $^{12}\text{C}$  or  $^{16}\text{O}$  scale. However, the value of the faraday is dependent on the atomic weight scale. On the  $^{12}\text{C}$  scale,  $F = 96,487 \approx 1.6$  coulombs.



**AMPERE.** The rate of flow of electrons is measured in **amperes**. One ampere is the flow of 1 coulomb/sec through a conductor. For a current strength of 1 amp (a rather weak current), 96,500 sec would be required for  $6.02 \times 10^{23}$  electrons (1 faraday) to pass by a given point in the circuit:

$$\text{coulombs} = \text{amperes} \times \text{seconds}$$

**OHM AND VOLT.** The atoms, molecules, and ions of substances offer a certain amount of resistance to the flow of electrons through them. The unit of resistance is the **ohm**; it is defined as the resistance offered by a uniform thread of mercury 106.3 cm long and containing 14.4521 g of mercury at 0°C. The *potential* (electrical pressure) required to cause a flow of 1 coulomb/sec through this thread of mercury is called a **volt**. A current with a potential of 96,500 volts would drive  $6.02 \times 10^{23}$  electrons (1 faraday) through this thread of mercury each second.

**WATT AND WATTHOUR.** The amount of energy delivered by an electric current depends on the number of electrons (coulombs or faradays) that flow through the circuit and also the driving force (voltage) behind the electrons. The unit of electrical energy, the **joule**, is defined as the energy produced by the flow of 1 coulomb at a potential of 1 volt:

$$\text{joules} = \text{coulombs} \times \text{volts}$$

Electrical power refers to the rate at which energy is supplied. By definition, a current that supplies 1 joule of energy per second has a power of 1 **watt**. One thousand watts equals one **kilowatt**:

$$\text{watts} = \frac{\text{coulombs}}{\text{seconds}} \times \text{volts}$$

$$\text{watts} = \text{amperes} \times \text{volts}$$

A 1,000-watt heating unit on an electric stove connected to its proper circuit uses 1,000 joules of electrical energy each second. When this stove is operated for 1 hr,  $1,000 \times 60 \times 60$ , or 3,600,000, joules of electrical energy is used. This amount of energy is called a **kilowatt-hour**; it costs home consumers from about 0.4 to 10 cents, depending on local rates. Ten ordinary 100-watt light bulbs burning for 1 hr will use this same amount of electrical energy.

## PRODUCTION OF ELECTRICITY BY CHEMICAL REACTIONS

### SPONTANEOUS CHEMICAL REACTION

Oxidation was defined in Chap. 6 as a reaction in which the oxidation state of an atom, molecule, or ion becomes more positive; and reduction as a reaction in which the oxidation state becomes less positive. All the reactions to be discussed in this chapter in connection with electrochemical changes are oxidation-reduction reactions;

and in all cases, the oxidation state changes because electrons are actually transferred, becoming more positive if electrons are lost and less positive (more negative) if electrons are gained. For the specific cases in which electrons are transferred from one particle to another, we may think of *oxidation as the loss of electrons by atoms, molecules, or ions*; and *reduction as the gain of electrons by these particles*. As a simple example of oxidation and reduction let us consider the reaction that occurs when a strip of zinc is immersed in a solution of copper sulfate (Fig. 18-1). There is a spontaneous reaction; metallic copper plates

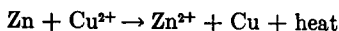
Electrons are spontaneously transferred from zinc atoms to copper ions.



out on the zinc strip, the zinc strip is gradually dissolved, and heat energy is liberated. The reaction may be formulated thus:



Actually, the reaction occurs between zinc atoms and copper ions:



When we inspect this equation, we see that each atom of zinc must lose 2 electrons to become a zinc ion, and each ion of copper must gain 2 electrons to become a copper atom:

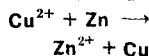
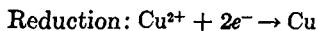
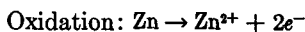


FIG. 18-1

Although this phenomenon is electrical in nature, no flow of electrons can be detected, because the copper ions touch the zinc atoms, and the electrons are transferred directly from the atoms to the ions.

The fact that this is a spontaneous reaction means there is a considerable driving force or potential behind the transfer of valence electrons from the zinc atoms to the copper ions. Actually this force is sufficient to cause the electrons to flow from the zinc atoms to the copper ions through a conductor.

## VOLTAIC CELL

In order for the reaction above to occur when the zinc is not in direct contact with the copper sulfate solution, provisions must be made for (1) the flow of electrons from zinc atoms to copper ions and (2) diffusion of the positive and negative ions so that the solution will remain essentially neutral.

There are several methods of providing for the diffusion of the ions. A common laboratory method is to immerse the zinc strip in a solution of a zinc salt, such as zinc sulfate, and to immerse a piece of copper in a solution of copper sulfate. The zinc sulfate solution is connected to the copper sulfate solution by a *salt bridge* (see Fig. 18-2),

# ELECTROCHEMISTRY; OXIDATION-REDUCTION EQUATIONS

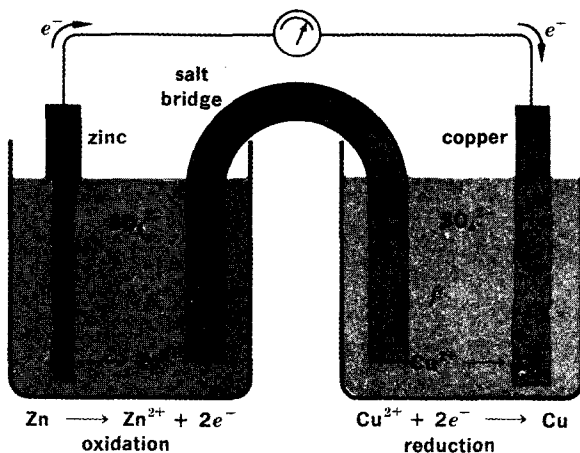
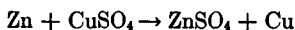


Diagram of one type of a voltaic cell.

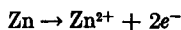
FIG. 18-2

which provides for the diffusion of the ions. The salt bridge is filled with a solution of an electrolyte that does not change chemically in the process. Potassium sulfate ( $K^+$ ,  $K^+$ ,  $SO_4^{2-}$ ) serves nicely for this purpose. Such salts as  $NaCl$ ,  $KCl$ , and  $KNO_3$  are also satisfactory.

When the reaction

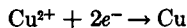


proceeds as indicated in Fig. 18-2, the action will continue till one of the reactants, that is, either the zinc atoms or the copper ions, is used up. Valence electrons will flow from the zinc atoms into the conducting wire, and the  $Zn^{2+}$  ions, as they form, will enter the solution and diffuse away from the zinc strip.



Negative ions will also diffuse through the salt bridge toward the zinc electrode. In time, it can be seen that the zinc strip is disappearing.

The electrons given up by the zinc atoms enter the connecting wire and cause electrons at the other end of the wire to collect on the surface of the copper electrode. These electrons react with copper ions to form copper atoms that adhere to the electrode as a copper plate:



In time, the metallic copper electrode increases in size and the blue color of the copper sulfate solution fades because of the decreasing concentration of the copper ions. The  $SO_4^{2-}$  ions that are left behind by the copper ions diffuse away from the copper electrode. The  $K^+$  ions also diffuse out of the salt bridge toward the copper electrode. Thus, while the reaction is in progress, there is an overall motion of negative ions toward the zinc strip and an overall motion of positive ions toward the copper electrode. The pathway for this directional

flow of ions through the solution may be thought of as the **internal circuit**, and the pathway for the flow of electrons through the conducting wire as the **external circuit**. Unfortunately, the internal circuit also provides a pathway by which the copper ions can reach the zinc atoms by diffusion. In time, therefore, the reaction will go to completion (and the battery will run down), even though the external circuit has not been closed.

Because the flow of electrons through the external circuit constitutes an electric current, we have harnessed the reaction between the zinc and copper sulfate so that a current of electricity will be produced. The energy that is given off as heat energy when these two react by direct contact is now evolved mostly as electrical energy. The apparatus and chemicals (Fig. 18-2) are referred to collectively as a **battery** or **voltaic cell**. The zinc strip is the negative electrode,<sup>1</sup> because electrons originate at it; the copper is the positive electrode, because electrons are attracted to it. A battery in which zinc and zinc sulfate and copper and copper sulfate are used is known as a Daniell cell, after its inventor. The voltage of the Daniell cell is about 1.1 volts, depending on the concentrations.

Electricity is not stored, as such, in this cell or any other voltaic cell, such as a flashlight battery or an automobile battery. These batteries provide for exothermic oxidation-reduction reactions in which the chemical change takes place by the transfer of electrons through an external circuit. Oxidation—that is, the loss of electrons—occurs at the negative electrode (anode); reduction occurs at the positive electrode (cathode).

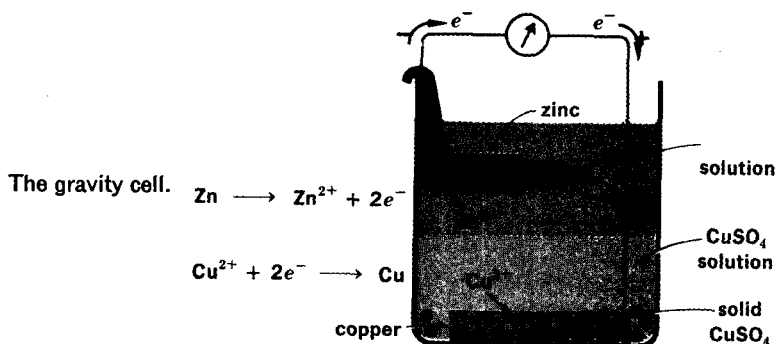


FIG. 18-3

**Gravity Cell.** Another way of utilizing the reaction between zinc and copper sulfate to supply a current of electricity is shown in Fig. 18-3. Metallic copper, immersed in a saturated solution of copper sulfate, serves as one of the electrodes. Because copper ions are re-

<sup>1</sup> The cathode is defined by some authorities as the electrode at which reduction occurs. By this definition, the cathode is the negative electrode in the electrolytic cell and the positive electrode in the voltaic cell.

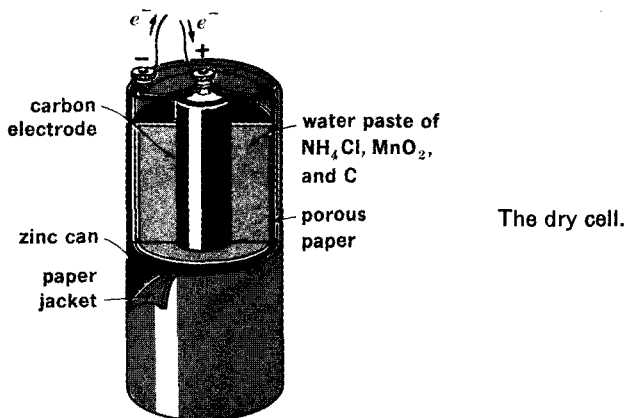


FIG. 18-4

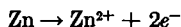
moved as the current is drawn from the battery, solid copper sulfate is placed in the bottom of the jar so that it will dissolve as needed. Floating on this dense solution of copper sulfate is a dilute solution of zinc sulfate in which is immersed a large piece of zinc metal. The zinc is branched in the form of a *crowfoot* to provide a large surface, and is quite heavy, because it will be used up as the battery provides current. The zinc is not in direct contact with the copper ions. No reaction can occur till the external circuit is closed, thus permitting the passage of electrons from the zinc to the copper ions.

No salt bridge is needed in the gravity cell, because the zinc sulfate solution is in direct contact with the copper sulfate solution, and ions can diffuse freely from one to the other, so that electroneutrality is maintained in each. The reactions at the two electrodes are identical with those in the Daniell cell. At one time the gravity cell was widely used as the source of electricity for telegraph instruments.

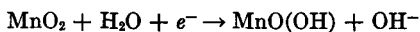
**Dry Cell.** The construction of the ordinary dry battery<sup>1</sup> used in flashlights and portable radios is shown in Fig. 18-4. Zinc metal again acts as the negative electrode and is also used as a container for the other components of the battery. The can is lined with moist porous paper that prevents the zinc from coming in contact with the other reactants but permits the diffusion of ions. The positive electrode is an inert carbon rod located in the center of the can. Surrounding this rod is a watery paste of manganese dioxide and ammonium chloride, with some carbon added to improve the conductivity. This cell is called "dry" because the amount of water is relatively small and the cell contents do not splash about. However, some moisture is essential to provide a solution for the diffusion of ions between the electrodes.

<sup>1</sup> The word *battery* was originally used to designate a *series* of voltaic cells, but it is now popularly used to denote any voltaic source of current, either a single dry-cell "battery" or the several cells of an automobile "battery."

When the cell is delivering current, the reaction at the negative electrode is one that involves the oxidation of zinc:



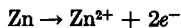
The reaction at the positive electrode appears to involve two or more reactions, depending in part on the conditions under which the cell is operated. If the cell is used for extremely short periods alternating with extended idle periods, the diffusion of reactants and products is such as to maintain fairly constant concentrations in the vicinity of the electrodes. On the other hand, if the cell is operated for longer periods and the idle periods are shorter, the concentrations change and the reaction changes accordingly. Under conditions of moderate use, hydrous manganous oxide,  $\text{MnO}(\text{OH})$  or  $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , appears to be the main reduction product. The reaction for its formation at the positive electrode is



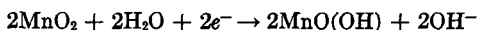
The  $\text{OH}^{-}$  ions may react with  $\text{NH}_4^{+}$  ions to form ammonia and water. Insoluble  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  is always present in large amounts in a run-down cell; its presence is accounted for by the fact that  $\text{NH}_3$  molecules, zinc ions, and chloride ions are brought together through diffusion.

When the cell is delivering moderate amounts of current, the reactions may be summarized thus:

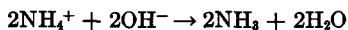
At - pole (anode):



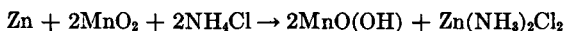
At + pole (cathode):



Nonoxidation-reduction reactions:



Overall reaction:



It is a familiar fact that, when a flashlight is used continuously for an hour or so, the light dims and the battery appears to be run down. After standing idle for some time, the battery again supplies the normal amount of current. The explanation is as follows. The idle period enables chemical reactions and diffusion processes to occur that remove reaction products from the immediate vicinity of the electrodes and permit the approach of fresh reactants.

A single dry cell has a voltage of 1.5. By connecting several in series, higher voltages are obtained.

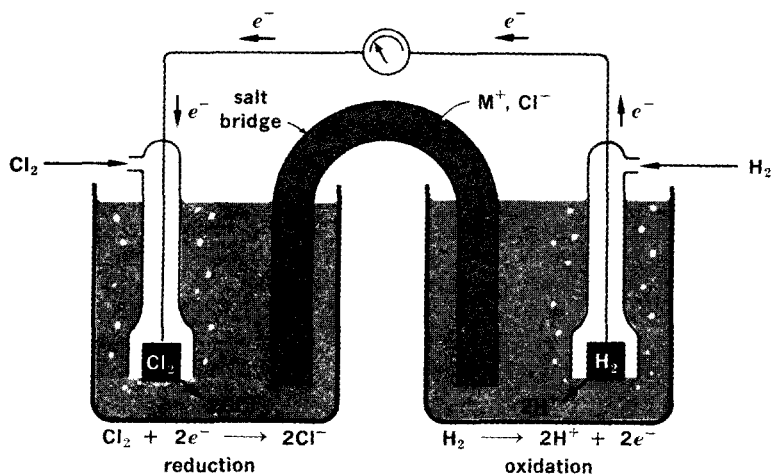


FIG. 18-5

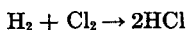
A voltaic cell which depends on the reactions of two gaseous elements.

### HYDROGEN ELECTRODE

No difficulties are encountered in making an electrode of one of the common metals; all that is necessary is to immerse a strip of the metal in a solution of its ions. However, building an electrode involving one of the gaseous elements and its ions presents more of a problem. Obviously, we cannot take a "piece" of gas, insert it in a solution of its ions, and connect a wire to it, thus making it part of a voltaic cell. Yet methods have been worked out that, in principle, accomplish just this. Elemental hydrogen, maintained in contact with a solution of its ions, can be made one electrode of a voltaic cell by the method shown in Fig. 18-5.

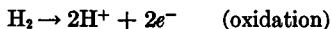
The **hydrogen electrode** consists of a skirted glass tube through which hydrogen gas can be continuously passed over a platinum foil (right electrode in Fig. 18-5). Coming down through the tube is a platinum wire that is connected to the platinum foil. The foil itself is covered with finely divided platinum to provide a large surface. Platinum adsorbs hydrogen; hence in effect the electrode is a core of platinum with an adsorbed film of hydrogen exposed to a solution that contains  $\text{H}^+$  ions, that is, an acid. When hydrogen is removed by the withdrawal of current from the cell, the film of it is constantly replenished from the hydrogen that passes through the glass tube. The platinum, being much less active than hydrogen, does not lose or gain electrons so long as hydrogen and hydrogen ions are present. The chlorine electrode, the other electrode in Fig. 18-5, is constructed in a similar manner.

In the voltaic cell shown in Fig. 18-5, the overall cell reaction is



When the battery is delivering current, hydrogen molecules give up electrons to form hydrogen ions, and chlorine molecules take up electrons to form chloride ions. The hydrogen electrode is the negative electrode, because electrons are originating at this point. The electrode reactions are:

At - pole (anode):



At + pole (cathode):



## STANDARD ELECTRODE POTENTIALS

The tendency of a substance to undergo oxidation or reduction reactions can best be expressed in terms of oxidation (or reduction) potentials. To do this, an electrode to be used for comparison is arbitrarily selected. This comparison electrode is used as half of a voltaic cell, the cell being completed with an electrode of the substance being compared. The voltage of this battery is read with a voltmeter. The magnitude of the voltage and the direction of the electron flow are indicative of the tendency of the substance to undergo oxidation by giving up electrons to the comparison electrode, or reduction by receiving electrons from the comparison electrode, as the case may be.

In actual practice, the hydrogen electrode is often used as the comparison electrode. This is fortunate for us, for our study of the preparation of hydrogen by the action of active metals on acids (Chap. 6) has given us an understanding of the tendency of metals to lose electrons to hydrogen ions.

Because temperature and concentration influence voltage, these variables must be held constant for the comparisons. The temperature is held at 25°C, the concentration of the ions in contact with the elemental electrodes is held at 1 molal,<sup>1</sup> and the gas pressure at 1 atm. Electrodes maintained under these conditions are called **standard electrodes**.

The comparisons are made in a voltaic cell set up like that in Fig. 18-6. Remember that, in these comparisons, the hydrogen electrode is always half of the cell and that the M electrode, the standard electrode of the element being compared, is the other half. If the M electrode is a standard copper electrode (a strip of copper immersed in a 1 molal solution of  $\text{Cu}^{2+}$  ions), the voltmeter will indicate a voltage of 0.337 volt. The reactions at the two electrodes are:

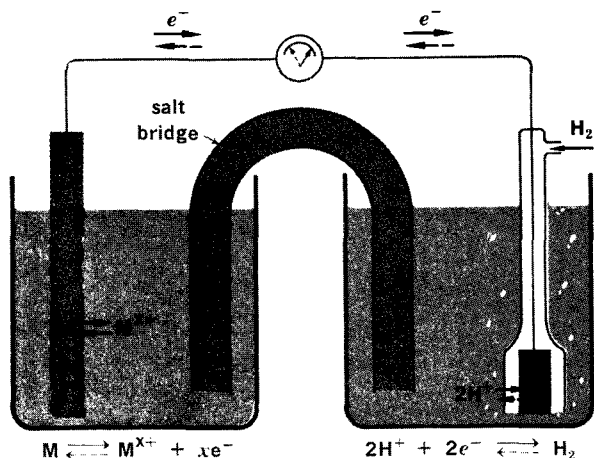
At - pole (anode):



<sup>1</sup> The ionic concentration is not precisely 1 mole per 1,000 g of solvent but is a concentration that behaves as an ideal 1 molal solution should behave.



# ELECTROCHEMISTRY; OXIDATION-REDUCTION EQUATIONS



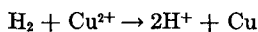
A voltaic cell for determining standard oxidation potentials.

FIG. 18-6

At + pole (cathode):



Cell reaction:

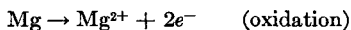


Because electrons originate at the hydrogen electrode, it is negative; the copper electrode is positive.

If the M electrode is a standard silver electrode, the voltage of the cell as indicated by the voltmeter will be 0.799 volt. The fact that this voltage is higher than the hydrogen-copper cell voltage indicates that silver ions have a greater tendency to undergo reduction (gain electrons) than copper ions do.

With an M electrode of magnesium, the deflection of the voltmeter is in the opposite direction; the reading is 2.37 volts. This opposite deflection means that magnesium atoms rather than hydrogen atoms are giving up electrons, and magnesium is acting as the negative electrode. Hydrogen, therefore, acts as the positive electrode, and the reactions are:

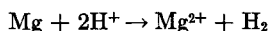
At - pole (anode):



At + pole (cathode):



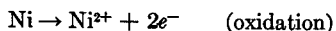
Cell reaction:



If the M electrode is nickel, the deflection of the voltmeter will be in the same direction as that obtained with a magnesium electrode;

the reading is 0.25 volt. This smaller voltage indicates that nickel has less tendency than magnesium to give up electrons to hydrogen ions. The reactions are:

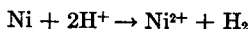
At - pole (anode):



At + pole (cathode):



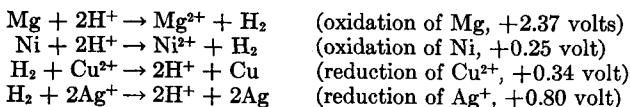
Cell reaction:



By comparing the voltage readings and the direction of current flow in the four cells described above, we can list the five elements—copper, silver, nickel, magnesium, and hydrogen—in a double column, with the most easily oxidized element at the top of one column and the most easily reduced ion at the bottom of the other column.

most easily oxidized	↑	Mg	$\text{Mg}^{2+}$	↓	most easily reduced
		Ni	$\text{Ni}^{2+}$		
		$\text{H}_2$	$\text{H}^+$		
		Cu	$\text{Cu}^{2+}$		
		Ag	$\text{Ag}^+$		

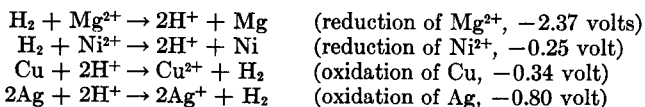
We now compare the overall reactions that occur spontaneously in the comparison cells:



Study of these equations indicates that:

1. Metals above hydrogen in activity undergo oxidation in the comparison cell. (The M electrode is the anode.)
2. Metal ions of metals below hydrogen undergo reduction in the comparison cell. (The M electrode is the cathode.)

We would infer that the reverse reactions below would not occur spontaneously in voltaic cells, but that they could be made to occur by passing a direct current of sufficient voltage through the cell, that is, by electrolysis:



Data such as the foregoing for Mg, Ni, Cu, and Ag have been determined for practically all of the elements. These data are recorded for some of the common elements in Table 18-1. Because they are abbreviated, we shall examine the table carefully.

1. The voltage of the entire cell has been assigned to the M elec-

**ELECTROCHEMISTRY; OXIDATION-REDUCTION  
EQUATIONS**

**TABLE 18-1**     *Standard oxidation potentials, E<sup>0</sup>*

anode*	anode reaction (oxidation)	oxidation potential, volts (standard hydrogen electrode = 0)
K;K <sup>+</sup>	$K \rightarrow K^+ + e^-$	+2.93
Ca;Ca <sup>2+</sup>	$Ca \rightarrow Ca^{2+} + 2e^-$	+2.87
Na;Na <sup>+</sup>	$Na \rightarrow Na^+ + e^-$	+2.71
Mg;Mg <sup>2+</sup>	$Mg \rightarrow Mg^{2+} + 2e^-$	+2.37
Al;Al <sup>3+</sup>	$Al \rightarrow Al^{3+} + 3e^-$	+1.66
Zn;Zn <sup>2+</sup>	$Zn \rightarrow Zn^{2+} + 2e^-$	+0.76
Fe;Fe <sup>2+</sup>	$Fe \rightarrow Fe^{2+} + 2e^-$	+0.44
Pb,PbSO <sub>4</sub> ;Pb <sup>2+</sup>	$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$	+0.36
Co;Co <sup>2+</sup>	$Co \rightarrow Co^{2+} + 2e^-$	+0.28
Ni;Ni <sup>2+</sup>	$Ni \rightarrow Ni^{2+} + 2e^-$	+0.25
Sn;Sn <sup>2+</sup>	$Sn \rightarrow Sn^{2+} + 2e^-$	+0.14
Pb;Pb <sup>2+</sup>	$Pb \rightarrow Pb^{2+} + 2e^-$	+0.13
D <sub>2</sub> ;D <sup>+</sup>	$D_2 \rightarrow 2D^+ + 2e^-$	+0.003
H <sub>2</sub> ;H <sup>+</sup>	$H_2 \rightarrow 2H^+ + 2e^-$	0.00
Cu;Cu <sup>2+</sup>	$Cu \rightarrow Cu^{2+} + 2e^-$	-0.34
I <sub>2</sub> ;I <sup>-</sup>	$2I^- \rightarrow I_2 + 2e^-$	-0.54
Hg;Hg <sup>2+</sup>	$Hg \rightarrow Hg^{2+} + 2e^-$	-0.79
Ag;Ag <sup>+</sup>	$Ag \rightarrow Ag^+ + e^-$	-0.80
Br <sub>2</sub> ;Br <sup>-</sup>	$2Br^- \rightarrow Br_2 + 2e^-$	-1.07
Cl <sub>2</sub> ;Cl <sup>-</sup>	$2Cl^- \rightarrow Cl_2 + 2e^-$	-1.36
PbO <sub>2</sub> ;Pb <sup>2+</sup>	$Pb^{2+} + 2H_2O \rightarrow PbO_2 + 4H^+ + 2e^-$	-1.46
Au;Au <sup>3+</sup>	$Au \rightarrow Au^{3+} + 3e^-$	-1.50
F <sub>2</sub> ;F <sup>-</sup>	$2F^- \rightarrow F_2 + 2e^-$	-2.65

\* The inert part, if any, of the electrode is not shown. For example, in the hydrogen and chlorine electrodes, platinum may be used as explained on page 474. Such electrodes may be represented as Pt,H<sub>2</sub>;H<sup>+</sup> and Cl<sup>-</sup>;Cl<sub>2</sub>,Pt, for anodes; and H<sup>+</sup>;H<sub>2</sub>,Pt, and Pt,Cl<sub>2</sub>;Cl<sup>-</sup>, for cathodes.

Because the most active elements, such as potassium and fluorine, react with water, water solutions cannot be used in constructing their electrodes; E<sup>0</sup> in such cases is determined indirectly, for example, by way of the relationship  $\Delta G^0 = -nFE^0$ .

trode and called the *standard oxidation potential*, E<sup>0</sup>. This is for comparison purposes only, because the potential of a single electrode cannot be measured. However, the hydrogen electrode is always half of each cell that is being compared. In each case therefore, the effect of the hydrogen electrode on the voltage is constant; the different voltages observed actually reflect the different tendencies of the M electrode to lose or gain electrons.

2. Only the anode or oxidation reaction is shown. When the electrode acts as the cathode and undergoes reduction, the reaction is the reverse of the one in the table.

3. Whether or not the anode reaction will occur spontaneously when the electrode is connected to a hydrogen electrode can be inferred from the sign of the oxidation potential in the table. If the sign is positive, the reaction will occur as written, and the electrode will act as the anode, the hydrogen electrode acting as the cathode. If the

sign is negative, the reverse reaction will occur spontaneously, and the hydrogen electrode will act as the anode (undergo oxidation).

4. When a hydrogen electrode acts as the cathode, the reaction is



When it acts as the anode, the reaction is



5. The oxidation potential decreases from +2.93 volts for potassium to -2.65 volts for fluorine. This means that there is a decreasing tendency from top to bottom to lose electrons (undergo oxidation) and an increasing tendency to gain electrons (undergo reduction).

## POTENTIALS OF VOLTAIC CELLS

From the oxidation potentials in Table 18-1, we can predict the voltage of any voltaic cell that consists of two standard electrodes listed in the table. Certain conventions used by electrochemists will be of value here; these are itemized below. We then show how the conventions are used to predict cell reactions, voltages for given combinations, and spontaneity of oxidation-reduction reactions.

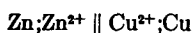
**Representation of a Voltaic Cell.** 1. To represent the anode (the electrode at which oxidation occurs), the solid phase is written first and the electrolyte last. The two are separated by a semicolon. (A vertical line is also commonly used.) The following examples illustrate this:

$\text{Zn}; \text{Zn}^{2+}$	an anode consisting of metallic zinc immersed in a water solution of zinc ions, for example, zinc sulfate, zinc chloride, or other salt of zinc
$\text{Pt}, \text{H}_2; \text{H}^+$	an anode consisting of solid platinum in contact with hydrogen—that is, hydrogen adsorbed on platinum—immersed in a water solution of hydronium ion, for example, an acid such as HCl or $\text{H}_2\text{SO}_4$

2. To represent the cathode (the electrode at which reduction occurs), the electrolyte is written first and the solid phase last. Examples:

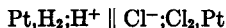
$\text{Cl}^-; \text{Cl}_2, \text{Pt}$	solid platinum cathode, with chlorine adsorbed on the platinum surface, immersed in a water solution of a chloride
$\text{Zn}^{2+}; \text{Zn}$	a cathode consisting of zinc immersed in a solution containing zinc ions

3. To represent the complete cell, the anode is written first and the cathode last. If a salt bridge is used, this is indicated by separating the two with two vertical parallel lines. Thus, the Daniell cell in Fig. 18-2 is represented by



## ELECTROCHEMISTRY; OXIDATION-REDUCTION EQUATIONS

A cell in which the overall reaction is  $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$  could be represented by



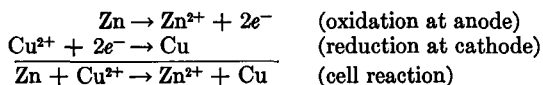
Use this mnemonic aid to keep track of the order:

solid; ions in solution  $\parallel$  ions in solution; solid

anode	cathode
(oxidation)	(reduction)

higher in Table 18-1      lower in Table 18-1

**CELL REACTION.** The *cell reaction* is the algebraic sum of the reactions that take place at the electrodes. The reaction at an electrode is frequently referred to as a *half-reaction*. For the cell  $\text{Zn}; \text{Zn}^{2+} \parallel \text{Cu}^{2+}; \text{Cu}$ , the half-reactions and cell reactions are



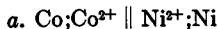
**VOLTAGE OF CELL.** The *voltage of the cell* is the algebraic sum of the oxidation potential and the reduction potential. (If we are dealing with standard electrodes the voltage is designated by  $E^0$ .) The voltage for the cell above is

$$\begin{aligned} E^0 &= E^0_{\text{oxidation}} + E^0_{\text{reduction}} \\ &= E^0_{\text{Zn}; \text{Zn}^{2+}} + E^0_{\text{Cu}^{2+}; \text{Cu}} \\ &= 0.76 \text{ volt} + 0.34 \text{ volt} \\ &= 1.10 \text{ volts} \end{aligned}$$

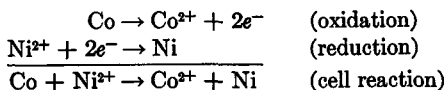
Note that  $E^0$  for the electrode at the left has the same sign as that given in Table 18-1 and that  $E^0$  for the electrode at the right has the sign opposite to that in the table. That is, reduction occurs at the latter electrode. Because Table 18-1 gives only oxidation potentials, the sign must be changed if a reduction potential is needed.

**Spontaneity of Reaction.** If the voltage of the cell as calculated above is positive, the cell reaction will take place spontaneously as written, and the cell will provide current. Finding that  $E^0_{\text{Zn}; \text{Zn}^{2+}} + E^0_{\text{Cu}^{2+}; \text{Cu}}$  gives a positive 1.10 volts reveals that  $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$  is a spontaneous exothermic process. Conversely,  $E^0_{\text{Cu}; \text{Cu}^{2+}} + E^0_{\text{Zn}^{2+}; \text{Zn}}$  gives a negative 1.10 volts, showing that the chemical reaction,  $\text{Cu} + \text{Zn}^{2+} \rightarrow \text{Zn} + \text{Cu}^{2+}$ , does not take place spontaneously.

**PROBLEM 1** For each of the following voltaic cells, write the half-reactions, designating which is oxidation and which is reduction; then write the cell reaction. Next, calculate the voltage of the cell made from standard electrodes.



**Solution** Half-reactions and cell reaction:

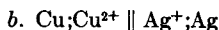


Voltage of cell:

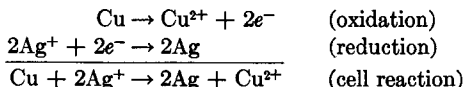
$$\begin{aligned} E^0 &= E^0_{\text{oxidation}} + E^0_{\text{reduction}} \\ &= E^0_{\text{Co};\text{Co}^{2+}} + E^0_{\text{Ni}^{2+};\text{Ni}} \end{aligned}$$

(Now refer to Table 18-1 for oxidation potentials; the reduction potential is opposite in sign to the oxidation potential.)

$$\begin{aligned} &= 0.28 \text{ volt} + (-0.25 \text{ volt}) \\ &= 0.03 \text{ volt} \end{aligned}$$

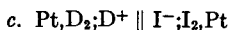


*Solution* Half-reactions and cell reaction:

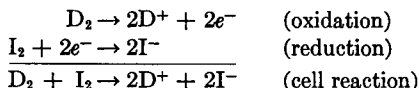


Voltage of cell:

$$\begin{aligned} E^0 &= -0.34 \text{ volt} + 0.80 \text{ volt} \\ &= 0.46 \text{ volt} \end{aligned}$$



*Solution* Half-reactions and cell reaction:



Voltage of cell:

$$\begin{aligned} E^0 &= 0.003 + 0.54 \\ &= 0.543 \text{ volt} \end{aligned}$$

(Note that, if ordinary hydrogen is used as the anode instead of heavy hydrogen, the voltage is  $E^0 = 0 + 0.54 = 0.54$  volt.)

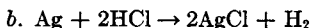
**PROBLEM 2** Represent the electrochemical cell based on each of the chemical reactions below. Then predict whether the cell could be used to supply current.



*Solution* Because the lead changes from an oxidation state of 0 to +2 (oxidation), our representation would show  $\text{Pb};\text{Pb}^{2+}$  as the anode. At the same time bromine changes from 0 to -1 (reduction). Hence the cell is represented thus:



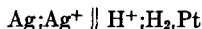
Table 18-1 shows that the sum of  $E^0_{\text{Pb};\text{Pb}^{2+}}$  and  $E^0_{\text{Br}_2;\text{Br}^-}$  has a positive value.<sup>1</sup> Hence, the reaction  $\text{Pb} + \text{Br}_2 \rightarrow \text{PbBr}_2$  proceeds spontaneously and could be used in a voltaic cell to supply current.



<sup>1</sup> Note that the order of designating  $E^0_{\text{reduction}}$  ( $E^0_{\text{Br}_2;\text{Br}^-}$ ) does not follow the order of designating the cathode ( $\text{Br}^-;\text{Br}_2;\text{Pt}$ ). In designating a cathode, the electrolyte (solution of  $\text{Br}^-$  ions) is shown first, and the solid phase ( $\text{Br}_2$  adsorbed on  $\text{Pt}$ ) is shown last. Because  $\text{Br}_2$  is being reduced to  $\text{Br}^-$  ion at this electrode, it is proper to write  $\text{Br}_2$  first for  $E^0_{\text{reduction}}$ .

## ELECTROCHEMISTRY; OXIDATION-REDUCTION EQUATIONS

*Solution* In this reaction silver atoms undergo oxidation to silver ions, and hydrogen ions undergo reduction to hydrogen molecules. The cell is written thus:



From Table 18-1 we see that the sum of the oxidation and reduction potentials is minus 0.80 volt. Hence, this reaction requires energy, and it could not be used to supply current.

### IMPORTANCE OF STANDARD ELECTRODE POTENTIALS

Most of the large number of voltaic cells that we could devise on the basis of standard electrode potentials would have no practical value. The real value of the data in Table 18-1 is that they provide a better understanding of all oxidation-reduction reactions, irrespective of whether they take place in the compartments of a battery, or by direct contact in a beaker in the laboratory, or in the cells of living organisms, or in huge vats in industrial processes. In all cases, electrons are being shifted about, and this table provides us with a comparison of the relative tendencies of different substances to acquire or to give up electrons. From the relative positions of the metals in Table 18-1 we would predict that, when a strip of magnesium is placed in a nickel chloride solution, a rather rapid oxidation-reduction would take place spontaneously, with the liberation of heat. Similarly, we would predict that, when metallic nickel is placed in a solution of magnesium chloride, no reaction would occur; that is, nickel atoms do not spontaneously give electrons to magnesium ions. This does not mean that such a reaction could not be made to occur. However, we could predict that it could occur only as a result of the expenditure of energy coming from an outside source; that is, the process would be endothermic.

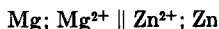
### FREE ENERGIES FROM ELECTRODE POTENTIALS

A major use of electrode potentials is in calculating the free energy changes,  $\Delta G$ , for chemical reactions. The change in the Gibbs free energy,  $\Delta G$ , for a process was defined in Chap. 16 as the maximum amount of useful work that can be done by that process. For a voltaic cell, the maximum amount of work available is calculated by multiplying the charge that is moved times the voltage that the charge is moved through. In the oxidation (or reduction) of one mole, the total charge is  $nF$ , where  $n$  is the number of electrons involved in the equation for the cell reaction and  $F$  is the value of one faraday of electricity. If the voltage is  $E$ , the maximum work that a cell can do per mole of chemical reaction is  $nFE$ . It follows that

$$\Delta G = -nFE$$

viously defined, in which a spontaneous reaction is denoted by a negative value of  $\Delta G$  or a positive value of  $E$ . If  $E$  has the units of volts and  $F$  is 96,500 coulombs, the value of  $\Delta G$  is given in joules of energy (4.184 joules = 1 cal).

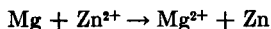
Consider the cell reaction



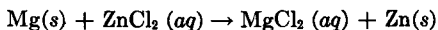
We calculate from Table 18-1 that  $E^0$  is  $2.37 - 0.76 = 1.61$  volts. Therefore,

$$\begin{aligned}\Delta G &= -(2)(96,500)(1.61) \text{ joules} \left( \frac{1 \text{ cal}}{4.184 \text{ joules}} \right) \\ &= -74,270 \text{ cal} = -74 \text{ kcal}\end{aligned}$$

To correlate this value with data given in Chap. 16, we note that the cell reaction is equivalent to the reaction



We can imagine this reaction taking place as magnesium metal reacts with, say, a standard 1 molal zinc chloride solution:



Using data from Table 16-6, and remembering that  $\Delta G_f^\circ$  for any element is zero, we can calculate  $\Delta G_r^\circ$  for this reaction by writing

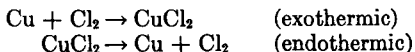
$$\begin{aligned}\Delta G_r^\circ &= \Delta G_f^\circ \text{ products} - \Delta G_f^\circ \text{ reactants} \\ &= (-172 + 0) - (0 - 98) = -74 \text{ kcal}\end{aligned}$$

## ELECTROLYSIS

The process whereby a current of electricity is used to bring about oxidation-reduction reactions that will not take place spontaneously is called electrolysis. Because electrolysis was discussed in Chap. 5 and in subsequent chapters, it will be considered here only briefly.

## DECOMPOSITION POTENTIALS

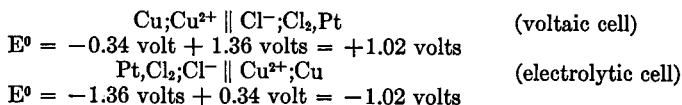
Let us start with two familiar reactions:



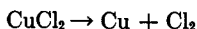
The transfer of electrons from copper atoms to chlorine atoms (the first reaction) occurs spontaneously and could be utilized to make a voltaic cell. The reverse (second) reaction, that is, the transfer of electrons from chloride ions to copper ions, occurs only if energy is supplied; the electrons have to be "pumped" from the one ion to the other. This can be done by forcing a direct current to pass through an electrolytic cell<sup>1</sup> in which the electrolyte is copper chloride.

<sup>1</sup> The cell that is used for electrolysis is called an electrolytic cell. Note that the lower unit in Fig. 18-7 is an electrolytic cell, and the three batteries at the top are voltaic cells. By one convention, the anode is the electrode at which oxidation occurs. Thus, the anode in the electrolytic cell is positive. (It is negative in the voltaic cell.)





A voltaic cell made up of standard copper and chlorine electrodes has a positive voltage of 1.02 volts. Now, if an outside current with a voltage slightly in excess of 1.02 volts is connected so as to oppose the discharge of the cell, the electrons will flow in the opposite direction; that is, the reverse reaction will occur (electrolysis of copper chloride):



Voltages smaller than 1.02 will not bring about the electrolysis of copper chloride. The minimum voltage required to bring about electrolysis is called the **decomposition potential**. It is apparent that the voltage required to decompose metallic salts of a given anion decreases progressively, the lower the metal in the activity series. (Because electrode potentials vary with concentration, the voltage required to decompose a molten salt is not the same as that required to produce electrolysis of this salt when in solution. Figure 18-7 illustrates one method of electrolytically decomposing salts of active metals.)

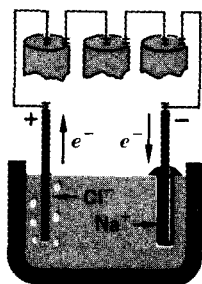
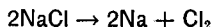


FIG. 18-7

Schematic representation of the electrolysis of molten sodium chloride:



## ELECTRODE PRODUCTS

It is not always easy or even possible to predict what products will result when a direct current is passed through an aqueous solution of an electrolyte. In addition to the ions from the electrolyte, water molecules and the ions from water ( $\text{H}^+$  and  $\text{OH}^-$ ) are present. These may also participate in the electrochemical reactions. Furthermore, the electrode products obtained with concentrated solutions often differ from those obtained with dilute solutions. To complicate the situation still more, one or both of the electrodes may react (the anode in Fig. 18-8 is one of the reactants). To narrow the list of variables, we shall select inert electrodes, usually platinum, and then state a few rules that enable us to predict electrode products for a considerable number of reactants.

At the inert cathode (—) the following occurs.

In silver plating base metals, the object to be plated is made the cathode (-); the anode (+) is made of pure silver.

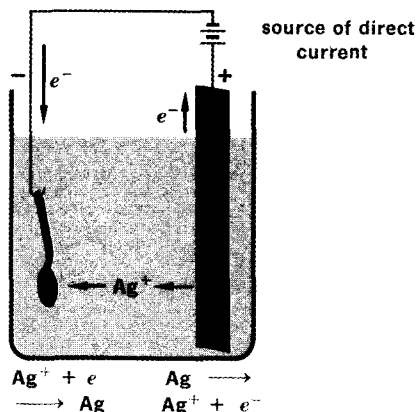


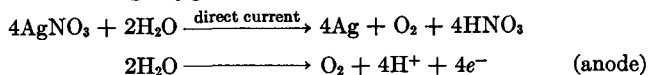
FIG. 18-8

1. If a metal is below hydrogen in activity, electrolysis of aqueous solutions of its salts causes the metal to form at the cathode. For example, if a water solution of  $\text{CuCl}_2$ , of  $\text{AgNO}_3$ , or of  $\text{HgCl}_2$  is electrolyzed, Cu, Ag, or Hg, respectively, will form.

2. If a metal is above hydrogen, electrolysis of aqueous solutions of its salts usually liberates hydrogen gas at the cathode. For example, if aqueous  $\text{NaCl}$ , or  $\text{KCl}$ , or  $\text{MgCl}_2$  is electrolyzed, hydrogen will be liberated at the cathode in each case.

At the inert anode (+):

1. Oxygen is liberated during the electrolysis of most salts with anions containing oxygen, such as  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . Example:



2. Anions such as  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  (but not  $\text{F}^-$ ) are more easily oxidized than water. Hence the free halogen is liberated. For example, during the electrolysis of concentrated sodium chloride, chlorine is liberated at the anode. In the case of dilute solutions, oxygen as well as chlorine is formed.

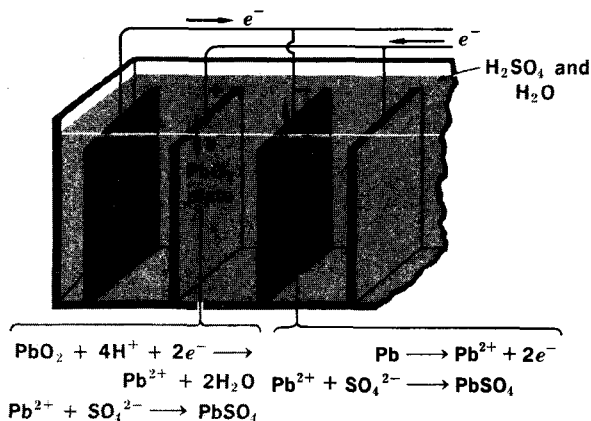
## ELECTROPLATING

In the manufacture of metallic articles, an article that is fabricated from metal or an alloy of metals is frequently covered with a thin plate of some other metal. This is generally done to protect it against corrosion and to make it more attractive.

One method of plating is by electrolysis. The article to be plated is the cathode, and a block of the plating metal is the anode. Both electrodes are immersed in an aqueous solution of a salt of the plating metal and connected to a source of direct current.

The plating of pure silver on a spoon made of a base metal is shown in Fig. 18-8. Many factors are involved in getting a plate of

## ELECTROCHEMISTRY; OXIDATION-REDUCTION EQUATIONS



Schematic representation of the lead storage battery.

FIG. 18-9

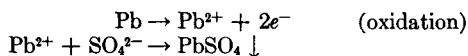
uniform thickness that adheres strongly to the base metal. Among the important variables that must be controlled are the cleanness of the surface to be plated, the voltage, the temperature and purity of the solution, the concentration of the ion being plated out, and the total concentration of ions in the solution.

### LEAD STORAGE CELL

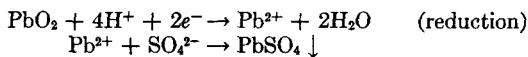
The storage battery of an automobile is both a voltaic and an electrolytic cell. When it is being used to start the car, it acts as a voltaic cell to supply electrical energy; while the motor is running, it functions as an electrolytic cell, receiving electricity from the generator, which restores, by electrolysis, the original reactants of the battery.

The lead storage battery is constructed of alternate plates of spongy lead and lead dioxide, separated by wood or glass-fiber spacers, and immersed in an electrolyte, an aqueous solution of sulfuric acid (Fig. 18-9). When the battery supplies current, the lead plate (Pb) is the negative pole and the lead dioxide plate (PbO<sub>2</sub>) is the positive pole. The following changes take place:

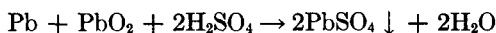
At the - pole (anode):



At the + pole (cathode):

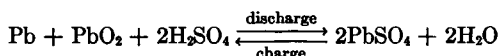


The complete reaction that occurs when current is drawn from the battery is given by the following equation:



Note that lead sulfate is formed at each electrode. Being insoluble, it becomes part of the electrode at which it forms, rather than dissolving in the solution. Note also that sulfuric acid is used up and water is formed. Because the diluted sulfuric acid is less dense than the original concentrated acid, the density of the electrolyte is commonly measured to determine the extent to which the battery is "run down."

Recharging the battery consists of "pumping" the electrons through the battery in the opposite direction; in other words, all the chemical changes above are reversed. The lead sulfate and water are changed back to lead, lead dioxide, and sulfuric acid:



When fully charged, a single cell of a lead storage battery has a potential of about 2.1 volts. The usual automobile battery has three or six of these cells connected in series and thus has a potential of 6 or 12 volts.

## FARADAY'S LAW

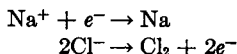
The passage of a current of electricity along a metallic conductor, such as a copper wire, involves no chemical reaction, but its passage through a solution of an electrolyte is achieved only by the loss and gain of electrons by the ions in the solution. Therefore the flow of electricity brings about a definite amount of chemical change in the electrolyte, the amount depending on the amount of electricity that passed through the circuit.

The experimentally determined fact that the amount of chemical change produced is directly proportional to the quantity of electricity passed was discovered by Michael Faraday before the electron nature of an electric current was known. Our knowledge today enables us to see the basis for this definite relationship. For example, when a current is flowing through molten sodium chloride, for each electron that enters from the cathode there must be a sodium ion,  $\text{Na}^+$ , to receive it; the sodium ion changes to an atom of sodium. Similarly, each electron that leaves at the anode comes from a chloride ion,  $\text{Cl}^-$ , with the resultant change of that chloride ion to an atom of chlorine. Therefore, the passage of one *faraday* ( $6.02 \times 10^{23}$  electrons) of electricity through molten sodium chloride is always accompanied by the formation of  $6.02 \times 10^{23}$  atoms (1 mole, 22.990 g) of sodium and the same number of chlorine atoms (1 mole, 35.453 g). However, this same amount of electricity passing through a water solution of copper chloride will plate out only one-half of this number of copper atoms (0.5 mole,  $63.54 \div 2$ , or 31.77 g), because each ion of copper,  $\text{Cu}^{2+}$ , gains two electrons when it changes to a copper atom. The weight of chlorine formed at the anode remains the same

## ELECTROCHEMISTRY; OXIDATION-REDUCTION EQUATIONS

as in the case of sodium chloride. It follows, then, that *during electrolysis, or while a voltaic cell is discharging, the passage of 1 faraday (96,500 coulombs) through the circuit is accompanied by the oxidation of 1 equivalent weight of matter at one electrode and the reduction of 1 equivalent weight at the other.* This is a statement of Faraday's law. The calculations in the following problems are based on this law.

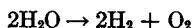
**PROBLEM 3** What weight of sodium and of chlorine will be formed when 10,000 coulombs of electricity is passed through molten sodium chloride? The electrode reactions are



*Solution* The equivalent weights (atomic weight  $\div$  change in oxidation state) of sodium and of chlorine are 22.990 and 35.453 g, respectively. Therefore, these amounts will be formed by the passage of 96,500 coulombs. The amounts formed by the passage of 10,000 coulombs will be

$$\begin{aligned}\frac{10,000 \text{ coulombs}}{96,500 \text{ coulombs}} \times 22.990 \text{ g} &= 2.38 \text{ g of Na} \\ \frac{10,000 \text{ coulombs}}{96,500 \text{ coulombs}} \times 35.453 \text{ g} &= 3.67 \text{ g of Cl}_2\end{aligned}$$

**PROBLEM 4** How much electricity will be required to decompose 1 lb (454 g) of water by electrolysis? The overall reaction is



*Solution* One mole of water (18 g) contains 2 equivalents of hydrogen (2 g) and 2 equivalents of oxygen (16 g). The equivalent weight of water is therefore 9 g. This weight of water will be decomposed by the passage of 1 faraday of electricity (yielding 1 g of hydrogen and 8 g of oxygen). To decompose 1 lb of water, the following amount of electricity is needed:

$$\frac{454 \text{ g}}{9 \text{ g}} \times 1 \text{ faraday} = 50.4 \text{ faradays}$$

## BALANCING OXIDATION-REDUCTION EQUATIONS

Simple oxidation-reduction equations, such as those which we have considered thus far in this chapter, can be balanced easily by inspection. The balancing of more complex equations can become time consuming unless a systematic method is followed. We shall discuss two schemes: the *oxidation-number method* and the *ion-electron method*. In either method, one must be able to assign oxidation numbers to the elements appearing in the equation. Preliminary to the development of the two schemes, then, let us review the assignment of oxidation states by working out the oxidation numbers for three examples, using the rules outlined on page 100.

**EXAMPLE 1**  $\text{K}_2\text{Cr}_2\text{O}_7$ : The oxidation numbers of K and O are +1 and -2, respectively. Because all the oxidation numbers for a neutral unit containing 2K, 2Cr, and 7O ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) must add to zero, we can write

$$2(+1) + 2(\text{Cr}) + 7(-2) = 0$$

$$2(\text{Cr}) = +12$$

$$(\text{Cr}) = +6, \text{ oxidation state of Cr in } \text{K}_2\text{Cr}_2\text{O}_7$$

$$+1 + 6 - 2$$

The oxidation states can be shown above the formula thus:  $\text{K}_2 \text{Cr}_2 \text{O}_7$

**EXAMPLE 2**  $\text{HPO}_4^{2-}$ : The oxidation state numbers must add to give the charge on the ion. Because in this type of ion, H and O have their usual oxidation states of +1 and -2, respectively, we can write

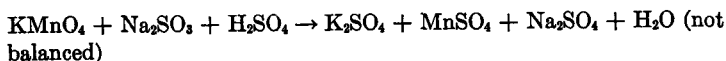
$$1(+1) + (\text{P}) + 4(-2) = -2$$

$$(\text{P}) = +5, \text{ the oxidation state of P}$$

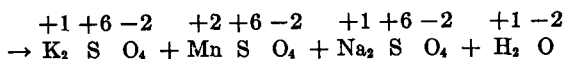
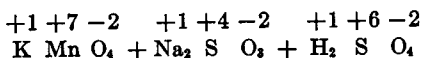
Oxidation numbers are arbitrarily assigned numbers and do not necessarily represent discrete charges. However, in the case of simple ions, the oxidation number and the charge on the ion have the same value. For  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Cu}^{2+}$ , and  $\text{S}^{2-}$  ions, for example, the oxidation numbers are +1, -1, +2, and -2, respectively.

### CHANGE IN OXIDATION-NUMBER METHOD

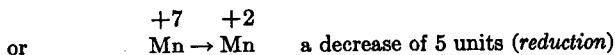
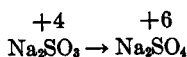
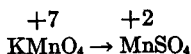
We shall illustrate this method by applying it to the balancing of the following equation:



*Step 1.* Assign the oxidation number of each element in the equation:

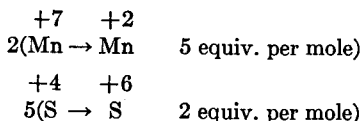


*Step 2.* Select the elements that undergo a change in oxidation number, that is, undergo oxidation or reduction. Determine the number of units of change in each:



*Step 3.* Use the numbers found in step 2 to determine the simplest ratio of moles of  $\text{KMnO}_4$  and  $\text{Na}_2\text{SO}_3$  that will provide equivalent quantities (Chap. 10).

## ELECTROCHEMISTRY; OXIDATION-REDUCTION EQUATIONS



That is, either 2 moles of  $\text{KMnO}_4$  or 5 moles of  $\text{Na}_2\text{SO}_3$  contains 10 equivalents, the former as an oxidizing agent, the latter as a reducing agent. These are the amounts needed to react completely with each other.

*Step 4.* Show 2 moles of  $\text{KMnO}_4$  and 5 moles of  $\text{Na}_2\text{SO}_3$  in the equation; also show the number of moles of products that result from the 2 moles of  $\text{KMnO}_4$  and 5 moles of  $\text{Na}_2\text{SO}_3$ :



*Step 5.* By inspection, determine the number of moles of the remaining substances,  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  in this case, required to balance the equation.

As the equation stands in step 4, 8 moles of sulfur is shown on the right ( $\text{K}_2\text{SO}_4$ ,  $2\text{MnSO}_4$ , and  $5\text{Na}_2\text{SO}_4$ ). To show the same amount on the left, 3 moles of  $\text{H}_2\text{SO}_4$  must be shown:



The amount of water may be deduced in two ways:

a. The total amount of oxygen atoms shown on the left of the last equation is 35 moles and on the right, not including  $\text{H}_2\text{O}$ , is 32 moles. Hence 3 moles of water must be shown.

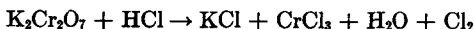
b. The amount of hydrogen atoms shown on the left is 6 moles ( $3\text{H}_2\text{SO}_4$ ). Hence, 3 moles of water must be shown.

The balanced equation is

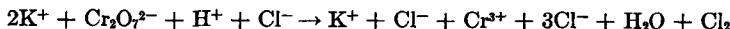


## ION-ELECTRON METHOD

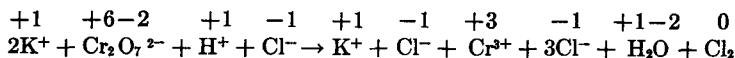
In many oxidation-reduction reactions, the chemical action involves relatively few ions of the several that may be present. For example, when either  $\text{NaMnO}_4$ ,  $\text{KMnO}_4$ , or  $\text{Ca}(\text{MnO}_4)_2$  is used as an oxidizing agent, the action probably involves the  $\text{MnO}_4^-$  ion only. The ion-electron method, then, focuses attention on the particles that actually participate in the oxidation-reduction reaction. We shall illustrate the method by applying it to balancing the following equation:



*Step 1.* Write the ionic equation for the reaction:<sup>1</sup>

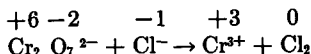


*Step 2.* Assign the oxidation numbers:



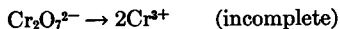
<sup>1</sup> It is sometimes difficult for the student to decide what ions exist in solution on the basis of the formula of the compound. The following system is used for most ionic compounds containing oxygen and two other elements. Consider  $\text{K}_2\text{Cr}_2\text{O}_7$  as an example. The first element in the formula forms a simple positive ion, for example,  $\text{K}^+$ ; the second element is combined with oxygen in an oxy-ion, for example,  $\text{Cr}_2\text{O}_7^{2-}$ .

Write down only those items which involve an element that changes in oxidation number:

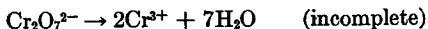


The chromium is reduced, because its oxidation state changes from +6 to +3. Some of the chlorine is oxidized (it changes from -1 to zero), but some of it is not changed.

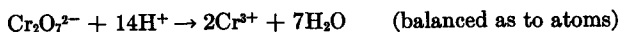
*Step 3.* For the reduction equation



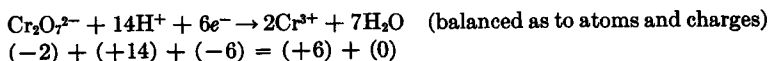
Then, knowing that the oxygen goes to form water, we have



And, knowing that hydrogen ions must join the oxygen to form water, we have



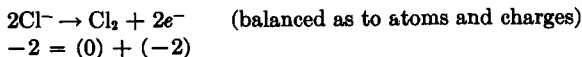
Adding enough electrons to the left side to balance the equation electrically gives



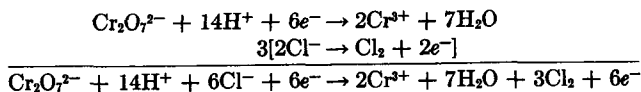
For the oxidation equation



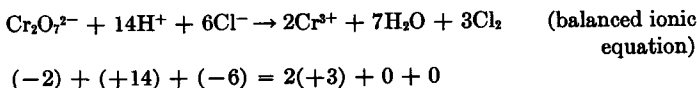
To balance this equation electrically,  $2e^-$  must be added to the right-hand side:



*Step 4.* Next, we wish to add a balanced reduction equation to a balanced oxidation equation. Multiply the second equation by 3 so that the number of electrons lost in oxidation equals the number gained in reduction; then add:



Next cancel electrons:



*Step 5.* In the ionic equation there is no mention of  $\text{K}^+$  ions. Nor are enough negative ions shown to make the net charges on both sides of the equation equal zero. To obtain a balanced overall equation, both of these omissions must be taken care of by including two  $\text{K}^+$  ions for each  $\text{Cr}_2\text{O}_7^{2-}$  and one  $\text{Cl}^-$  for each  $\text{H}^+$  in writing the overall balanced equation. The final equation is





## CHAPTER REVIEW

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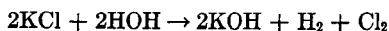
### Terms

Coulomb, faraday, ampere, ohm, volt, watt, joule, voltaic cell, internal and external circuits, battery, dry cell, hydrogen electrode, standard electrode potential,  $E^\circ$ , electrolysis, decomposition potential, electroplating, lead storage cell, Faraday's law, oxidation and reduction equations,  $\Delta G = -nFE$ .

### Exercises

1. What is the rate of electron flow per second at a current of 1 amp?
2. Calculate the number of electrons that flow per second through a 7-watt flashlight bulb operating at 6 volts.
3. For each of the following, name an appropriate electrical unit: energy, potential, power, rate, amount of electricity.
4. Consider the description of the zinc-copper sulfate reaction described early in the chapter, and tell what you conclude about the change in free energy for this reaction.
5. Define anode and cathode in terms of oxidation and reduction.
6. Using mercury and iron, and any chemicals needed, show with a diagram how a cell similar in purpose to the Daniell cell could be constructed.
7. Solid  $\text{CuSO}_4$  is placed in the bottom of a gravity cell. Why?
8. Historically the gravity cell is of interest, and it illustrates some principles of cell design, but it was entirely too limited in its utility. Why? Contrast the possible use of a series of gravity cells with that of lead storage cells for use in automobiles.
9. When used continuously, voltaic cells, such as the flashlight battery and the automobile battery, appear to be run down. After standing for a period of time they become reactivated to some extent. Explain what happens.
10. If it were practical to recharge a dry cell, how could it be done? What reactions would take place?
11. How are the conditions for measuring standard electrode potentials related to those for measuring standard thermochemical data, such as enthalpies?
12.
  - a. This chapter has presented designs for electrodes involving gaseous elements as well as electrodes involving solid elements, both types of elements being in contact with solutions of their ions. Suggest a design for an electrode involving a liquid, such as mercury. Complete the design by showing how the mercury electrode could be utilized to make a voltaic cell based on the reaction  $\text{Hg} + \text{Cl}_2 \rightarrow \text{HgCl}_2$ . Label the anode and cathode.
  - b. Write the anode reaction, the cathode reaction, and the cell reaction.
  - c. Calculate the voltage of the cell if it is made of standard electrodes.

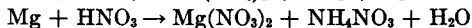
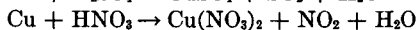
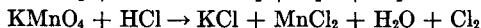
13. Show how a cell could be constructed with one ordinary hydrogen electrode and one deuterium electrode. Write the equations for the anode and cathode reactions, and indicate the direction of electron flow in the external circuit.
14. Represent in the conventional fashion the standard cells in which the following overall reactions are occurring spontaneously:
- $\text{Ni} + 2\text{H}^+ \rightarrow \text{Ni}^{2+} + \text{H}_2$
  - $\text{H}_2 + 2\text{Ag}^+ \rightarrow 2\text{Ag} + 2\text{H}^+$
  - $3\text{Ag} + \text{Au}^{3+} \rightarrow \text{Au} + 3\text{Ag}^+$
15. The voltage of a cell made with standard electrodes of palladium and zinc is 1.75 volts. Assuming that palladium ions ( $\text{Pd}^{2+}$ ) undergo reduction, write the equation for a reaction involving palladium that could be entered in Table 18-1, and assign to it the proper oxidation potential.
16. Represent in the conventional fashion the standard cells in which the following reactions could occur.
- $2\text{Al} + 3\text{CoCl}_2 \rightarrow 2\text{AlCl}_3 + 3\text{Co}$
  - $\text{Cu} + \text{FeCl}_2 \rightarrow \text{CuCl}_2 + \text{Fe}$
  - $\text{Ni} + \text{CoBr}_2 \rightarrow \text{NiBr}_2 + \text{Co}$
  - $\text{Hg} + 2\text{AgNO}_3 \rightarrow \text{Hg}(\text{NO}_3)_2 + 2\text{Ag}$
17. For each of the reactions in Exercise 16:
- Write equations for the half-reactions.
  - Calculate  $E^\circ$  for each cell, and state whether the cell is a voltaic or an electrolytic cell.
18. Choose the proper chemicals for constructing a battery of four cells, all alike, that will produce a voltage between 6.0 and 6.6 volts. Diagram the equipment, show the chemicals involved, and show the direction of electron flow.
19. *a.* Consider the electrolysis with platinum electrodes of a mixture of HCl and DCl solutions. Which would tend to be evolved more readily from the standpoint of voltage alone,  $\text{H}_2$  or  $\text{D}_2$ ?
- b.* Consider the reaction of iron with a mixture of HCl and DCl solutions. Which would tend to be evolved more readily from the standpoint of oxidation potentials,  $\text{H}_2$  or  $\text{D}_2$ ?
- c.* What important use could be made of the principle illustrated in (a)?
20. Silver or copper are easily electroplated on to articles from aqueous salt solutions; nickel or tin can also be deposited in this way, but not aluminium or magnesium. Discuss these facts, bearing in mind that the solutions can be of any possible concentrations.
21. Calculate the number of faradays and coulombs of electricity necessary to produce 1 mole each of the following:  $\text{Br}_2$  from  $\text{Br}^-$  solution; Pb from  $\text{Pb}^{2+}$  solution; Pb from  $\text{Pb}^{4+}$  solution; Au from  $\text{Au}^{3+}$  solution.
22. Calculate the weight and the volume of hydrogen and of chlorine that will be formed by passing 10,000 coulombs of current through a water solution of potassium chloride. The equation is



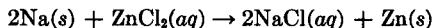
**ELECTROCHEMISTRY; OXIDATION-REDUCTION  
EQUATIONS**

23. How long will it take for a current of 3.00 amp to produce 1.00 g each of the following:  $H_2$  from  $H^+$  solution; Au from  $Au^{3+}$  solution; Sn from  $Sn^{2+}$  solution; and Sn from  $Sn^{4+}$  solution?
24.
  - a. A current from a supposedly constant source was passed through a solution of silver nitrate,  $AgNO_3$ , for 1 hr, depositing 6.581 g of silver. Calculate the number of faradays passed and the rate of flow in amperes.
  - b. If the current actually fluctuated, how would the accuracy of the calculations in (a) be affected?
25.
  - a. A current rated at 3.0 amp was passed through a  $Au^{3+}$  solution for 30 min. What weight of gold should be plated out?
  - b. If the measured weight of gold plated out under the conditions in (a) is 3.4 g, what is the efficiency of this process?
26. A liter of hydrogen gas is desired for an experiment. How long will it take to generate it by passing a current of 5.0 amp through hydrochloric acid?
27. How does the density of the electrolyte indicate whether a lead storage battery is charged or discharged?
28. In all the batteries that we have studied except the lead storage battery, special provisions were made to prevent certain ions from coming in direct contact with certain electrodes. How was this achieved in the gravity cell; in the flashlight battery; in the comparison cell? Why are no special provisions necessary in the lead storage cell?
29.
  - a. A solution of a metal in an unknown oxidation state was electrolyzed at 0.268 amp for 30.0 min, resulting in the plating out of 0.266 g of metal on the cathode. Calculate the equivalent weight of the metal.
  - b. If the specific heat of the metal in (a) is 0.0565 cal/(g  $\times$  deg C), what is its oxidation state and atomic weight?
30. Why is a direct current rather than an alternating current used for electroplating?
31. Calculate the cost of using a 1,200-watt room heater for 6.0 hr if electricity costs 1.3 cents/kwhr.
32. Give a logical explanation for each of the following:
  - a. An equivalent quantity of a 0.1 N solution of acetic acid conducts less electricity in a unit of time than 0.01 N acetic acid when each is placed between large electrodes that are 1 cm apart.
  - b. A solution of hydrogen chloride in benzene is a much poorer conductor than a solution of hydrogen chloride in water.
  - c. Pure molten potassium chloride is a much better conductor than solid potassium chloride.
  - d. When zinc metal is placed in a beaker containing a dissolved zinc salt, and silver metal is placed in a second beaker containing a dissolved silver salt, and the two metals are connected with a silver wire, no appreciable amount of current flows through the silver wire.
  - e. The electrical energy to plate out 1 mole of Zn from  $Zn^{2+}$  costs more than the electrical energy to plate out 1 mole of Cu from  $Cu^{2+}$ . In each case 2 faradays is consumed.

- f. If zinc is burned in an atmosphere either of chlorine, or of fluorine, or of sulfur, or of oxygen, it is said to be oxidized.
- g.  $E^\circ$  of the hydrogen electrode is zero.
- h. During the electrolysis of molten sodium chloride, sodium is liberated at the negative electrode; when aqueous sodium chloride is electrolyzed, hydrogen is liberated at the negative electrode.
- i. More heat is evolved when hydrogen burns in chlorine than in bromine.
33. Predict what is liberated at each electrode when aqueous solutions of the following are electrolyzed between inert electrodes:  $\text{H}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{CuSO}_4$ ,  $\text{KCl}$ ,  $\text{AuCl}_3$ ,  $\text{KF}$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Na}_3\text{PO}_4$ .
34. Indicate the ions and their relative numbers that probably exist in aqueous solutions of each of the following salts:  $\text{FeSO}_4$ ,  $\text{CaSeO}_3$ ,  $\text{KClO}_4$ ,  $\text{Na}_3\text{AsO}_3$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{Mg}(\text{MnO}_4)_2$ ,  $\text{NaMnO}_4$ ,  $\text{Bi}_2(\text{SO}_4)_3$ ,  $\text{Na}_3\text{NbO}_4$ ,  $(\text{NH}_4)_2\text{SO}_3$ , and  $\text{BaCrO}_4$ .
35. Assign an oxidation state to each element in the compounds listed in Exercise 34.
36. Balance the following equations, writing partial oxidation and reduction equations for each. The first three will be found balanced in Chap. 21, the next in Chap. 22, and the last two in Chap. 23:



37. Balance the following equations, writing partial oxidation and reduction equations for each:
- a.  $\text{Fe} + \text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{H}_2$
- b.  $\text{S} + \text{HNO}_3 \rightarrow \text{SO}_2 + \text{H}_2\text{O} + \text{NO}$
- c.  $\text{Cl}_2 + \text{H}_2\text{SeO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SeO}_4 + \text{HCl}$
- d.  $\text{KClO}_3 \rightarrow \text{KClO}_4 + \text{KCl}$
- e.  $\text{HClO}_2 \rightarrow \text{ClO}_2 + \text{Cl}_2 + \text{H}_2\text{O}$
- f.  $\text{Cu}_2\text{S} + \text{O}_2 \rightarrow \text{Cu}_2\text{O} + \text{SO}_2$
- g.  $\text{Na}_3\text{AsO}_3 + \text{I}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_3\text{AsO}_4 + \text{HI}$
38. Calculate the free energy change in kilocalories per mole of palladium for the cell reaction described in Exercise 15.
39. From the free-energy data in Table 16-6 calculate the voltage of a cell involving the following reaction; compare your answer with that calculated from the data in Table 18-1:



40. From indirect measurements and Hess's law type of calculations, a standard free energy change of  $-86.0$  kcal is calculated for the reaction



- a. Calculate the voltage of a standard cell in which this reaction occurs.

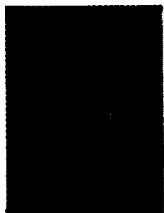
## ELECTROCHEMISTRY; OXIDATION-REDUCTION EQUATIONS

- b. Write the equation for a reaction involving cesium that could be entered in Table 18-1, and assign to it the proper oxidation potential.
41. Suppose you wished to determine the change in entropy associated with the reaction  $\text{Ni} + \text{CuSO}_4(\text{aq})$ . Describe the experimental measurements that you would make and the calculations necessary.

## SUPPLEMENTARY READING

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**METALS:****CHEMICAL PROPERTIES****AND COMPOUNDS****SYSTEMATIC STUDY OF INORGANIC  
CHEMISTRY**

The six chapters beginning with this one are concerned with the subject of inorganic chemistry. The arrangement of the elements in the periodic table is a guide to family and group relationships that unify and clarify this broad field of chemistry. Fortunately, a number of the families are similar enough to be discussed together. This is particularly true of the metals, which comprise about three-fourths of the elements.

In this chapter we discuss groups IA and IIA and then proceed to the transition metals and their neighbors, taking up several families together. In Chap. 20 we look at the production of metals from natural sources and the uses of important metals and alloys. In Chap. 21 to 24 the nonmetals are discussed a group at a time, beginning with group VIIA and working to the left in the periodic table.

Before taking up the chemistry of particular families, let us first review the division of the periodic table into general areas and examine some of the trends in behavior exhibited in the periods and groups of the table.

*General Divisions of the Periodic Table.* The elements can be divided into four major classes, each with important physical and chemical characteristics. These classes occupy four reasonably distinct areas on the long-form periodic table.

**NOBLE ELEMENTS.** The six elements that comprise group VIIIA are known as the **noble elements** or **noble gases**. They are colorless,

## METALS: CHEMICAL PROPERTIES AND COMPOUNDS

monatomic gases whose atoms show little tendency to gain or lose electrons. Their electronegativities are not well established, because so few compounds of the noble gases are known.

**METALS.** About eighty elements are classified as metals, including some from every group except VIIA and VIIIA. These elements are at the left and in the center of the periodic table.

In chemical reactions, the atoms of metals tend to donate electrons. Their electronegativities are low, ranging from about 2.2 down. An important property of metals with very low electronegativities is that their oxides react with water and yield  $\text{OH}^-$  ions. Metal oxides that act in this way are called *basic oxides*, because they are good proton acceptors and because in water they form the proton acceptor ion,  $\text{OH}^-$ . Metals whose hydrated oxides are *acidic* in water solutions are called *metallo-acid elements*.

**NONMETALS.** The nonmetals, consisting of about a dozen relatively common and important elements, are to the right on the periodic table, with the exception of hydrogen. These elements are characterized by their lack of the metallic properties in the solid state: they are, with few exceptions, nonconductors, nonmalleable, nonductile, and have no metallic luster. The nonmetals that are gases under normal conditions are composed of diatomic molecules.

The atoms of the nonmetals tend to accept electrons in chemical reactions with metals, but they also readily react with one another by forming covalent bonds, for example in  $\text{SO}_3$ ,  $\text{CO}_2$ ,  $\text{CCl}_4$ , and  $\text{H}_2\text{O}$ .

Electronegativities of nonmetals range from about 2.2 to 4.0. An important property is that nonmetal oxides react with water and yield  $\text{H}_3\text{O}^+$  ions. Nonmetal oxides are *acidic oxides*.

Hydrogen is classed by some chemists in subgroup IA, by others in subgroup VIIA (see also Fig. 4-15). One reason for this is that toward some elements it acts as an electron donor (like a metal) and toward other elements it acts as an electron acceptor. With an intermediate electronegativity of 2.1, it is between the metals and nonmetals in this respect. Because of its physical characteristics and the types of compounds it forms, hydrogen is known as a nonmetal.

**BORDERLINE ELEMENTS.** Borderline elements are elements that to some extent exhibit both metallic and nonmetallic properties; they usually act as electron donors with nonmetals and as electron acceptors with metals. Chemists do not agree as to exactly which elements should be included in this class, but they do agree that such elements lie close to the zigzag line in the periodic table inside the front cover. The names of some of these elements are boron, B, silicon, Si, germanium, Ge, and tellurium, Te. They are all solids at room temperature, somewhat brittle, and rather poor conductors of heat and electricity.

The electronegativities of the borderline elements range between 1.8 and 2.1. Their oxides react with water to yield solutions that are either weakly acidic or weakly basic.

**The Periodic Table and Trends in Behavior.** Perhaps the most important use of the table in predicting chemical properties is based on the relations between chemical properties and the structures of atoms. It will be helpful to refer to Figs. 4-15 and 19-1 as we take up each of the following trends in behavior.

**Trend 1.** There is a tendency for atoms to become smaller from left to right in a period. Because the increase in the positive charge on the nucleus exerts a continually greater attraction and because the screening effect (see Chap. 4) is not increasing so rapidly, the electrons are pulled in closer to the nucleus.

There is a great increase in size with the addition of an *s* electron to start a new main energy level (see Li, Na, K, Rb, and Cs). Note, however, that the minimum size is reached near the middle of the long periods and that there is even a slight increase in size toward the middle-right side. In periods 5 and 6, indium (In, 49) and thallium (Tl, 81), respectively, are seen to be slightly larger than their neighbors. This is apparently related to the fact that with these elements the *5p* and *6p* sublevels begin to be filled (see Fig. 3-14). Starting with yttrium (Y, 39) and lanthanum (La, 57), respectively, the elements in these two periods are adding electrons in inner levels; with indium and thallium, electrons again are added to the outside main levels, 5 and 6, respectively.

Toward group VIIIA in each period, the sizes of atoms decrease.

**Trend 2.** The tendency of atoms in A families to gain electrons increases from left to right in a period. The smaller the atom, the closer a valence electron can come to the positive nucleus, and the more tightly it is held. The weakness in applying this trend to the electronegativities of B families is indicated by Fig. 19-1.

**Trend 3.** The tendency for atoms to lose electrons increases from top to bottom in an A family.<sup>1</sup> A tabulation of the electronegativity of elements in a few representative families shows this trend clearly. These data are listed in Table 4-3 and plotted in Fig. 4-13.

**TRANSITION SERIES.** In the long periods the regular addition of electrons to *d* sublevels begins with the third element in the period and continues till the eighth element from the end is reached (that is, family IB). Examine the electron arrangements of scandium, Sc, and yttrium, Y, in periods 4 and 5 (see periodic table inside the front cover). In these cases the electron that was added as a result of the increase in atomic number went into the main energy level next to the outer-most one, that is, into a *3d* or *4d* orbital, respectively. In the elements after scandium and yttrium a *d* sublevel is built up from atom to atom roughly as the atomic number increases, till it contains its maximum of 10 electrons. The elements in a series in

<sup>1</sup> In some families the trend is just the reverse. For example, group IB consists of Cu, Ag, and Au, of which copper loses its electrons most easily; and group IIB consists of Zn, Cd, and Hg, of which zinc has the greatest tendency to lose electrons. Both gold and mercury are relatively inactive electron donors.



**METALS: CHEMICAL PROPERTIES  
AND COMPOUNDS**

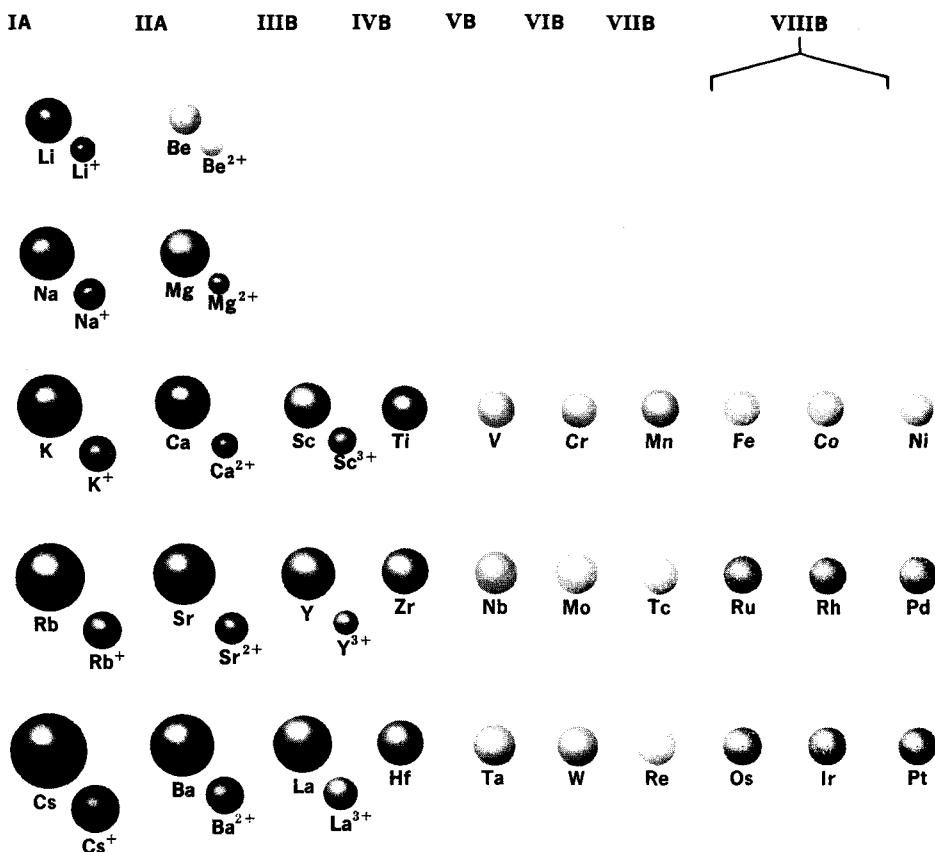


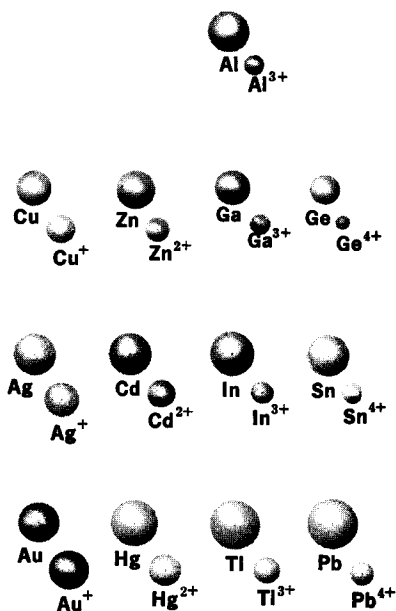
FIG. 19-1

which electrons are being added to *d* orbitals are called *transition elements*. (See Fig. 3-14.)

**INNER TRANSITION SERIES.** The third elements in periods 6 and 7 (lanthanum, La, and actinium, Ac) have outer electron configurations similar to those of scandium and yttrium. But with the fourth element in each of these last two periods, a series of fourteen elements begins in which the electron configurations of the outer two main levels remain very nearly constant. With cerium, Ce, begins a series in which electrons are added to the seven *4f* orbitals of the fourth main energy level. (See Fig. 3-14.) A similar series is apparently developed beginning with thorium, Th, in the seventh period, in which *f* electrons are added in the fifth main level (thorium itself being an exception). These two series, the *lanthanide series*<sup>1</sup> in the sixth period and the *actinide series* in the seventh period, are called *inner transition series*.

According to the most widely accepted theory, the actinide series

<sup>1</sup> The elements of the lanthanide series were for many years referred to as the *rare earths*.



The relative sizes of metal atoms and ions. (See also Fig. 4-15.)

ends with element 103, at which point the  $5f$  orbitals are filled. Element 104 should be a member of group IVB, being placed in the periodic table just under hafnium, number 72.

## ALKALI AND ALKALINE EARTH METALS

The alkali family of metals, located in group IA of the periodic table, consists of lithium, sodium, potassium, rubidium, cesium, and francium. The alkaline earth family, the group IIA elements, includes beryllium, magnesium, calcium, strontium, barium, and radium. The families are so named because their oxides and hydroxides are among the strongest bases (alkalis) known. In discussing these two families, particularly in describing trends and extremes in behavior, it is understood that francium and radium are not included; owing to their relative rarity and radioactivity many of their properties have been little studied.

**METALS: CHEMICAL PROPERTIES  
AND COMPOUNDS**

**TABLE 19-1**     *Physical properties of alkali metals (excluding francium)*

	Li	Na	K	Rb	Cs
melting point, °C	180	98	63	39	29
boiling point, °C	1326	889	757	679	690
density, g/ml	0.53	0.97	0.86	1.53	1.90
electron distribution	2,1	2,8,1	2,8,8,1	2,8,18,8,1	2,8,18,18,8,1
ionization energy, volts	5.39	5.14	4.34	4.18	3.89
atomic radius, Å	1.22	1.57	2.02	2.16	2.35
ionic radius, Å	0.60	0.95	1.33	1.48	1.69
electronegativity	1.0	0.9	0.8	0.8	0.7

**PHYSICAL PROPERTIES**

In Tables 19-1 and 19-2 are listed some of the important physical properties of the elements in groups IA and IIA, respectively. The elements in both of these families have the silvery luster of typical metals on freshly cut surfaces, but they tarnish rapidly on exposure to air. They also have the high electrical and thermal conductivities characteristic of metals.

Some of the properties of these elements not usually associated with metals are their relatively low melting points, their relatively low densities, and their softness. These three properties are especially typical of the alkalis, one of these metals being a liquid at room temperature and three having densities less than that of water. All of them, from lithium to cesium, can be easily deformed by squeezing between thumb and forefinger (with proper protection for one's skin). The alkaline earth elements are somewhat harder, ranging from barium, which is about as hard as lead, to beryllium, which is hard enough to scratch most other metals.

An understanding of the data in the latter part of Tables 19-1 and 19-2 is prerequisite to understanding the chemical behavior of the two families. The electronic structure is of prime interest. The relative simplicity of the chemical reactions of groups IA and IIA is associated with their simple electronic structures. Outside a stable core structure

**TABLE 19-2**     *Physical properties of alkaline earth metals (excluding radium)*

	Be	Mg	Ca	Sr	Ba
melting point, °C	1280	650	850	770	704
boiling point, °C	2970	1120	1487	1384	1638
density, g/ml	1.86	1.74	1.55	2.6	3.59
electron distribution	2,2	2,8,2	2,8,8,2	2,8,18,8,2	2,8,18,18,8,2
ionization energy, volts	9.32	7.64	6.11	5.69	5.21
atomic radius, Å	0.89	1.36	1.74	1.91	1.98
ionic radius, Å	0.31	0.65	0.99	1.13	1.35
electronegativity	1.5	1.2	1.0	1.0	0.9

similar to that of a noble element, they have, respectively, one or two  $s$  electrons that are lost relatively easily.

The elements in Groups IA and IIA have the lowest average ionization energies and electronegativities of all the families of elements. These properties are related to the sizes of the atoms (Fig. 19-1) and the relatively great distances from the nuclei of the outer  $s$  electrons.

**Flame Spectra.** As pointed out in Chap. 3, the elements of groups IA and IIA impart characteristic colors to an ordinary flame. In analytical laboratory work, flame tests are often used to reveal the presence of various alkali and alkaline earth elements. The yellow flame test for sodium is one of the most sensitive, 1 part of sodium in 10,000,000 parts of solvent being detectable.

## CHEMICAL PROPERTIES

**Activity.** The most striking characteristic of these elements is their extreme activity. The reason that most people are not familiar with the appearance of the very common metals sodium, potassium, and calcium is that these metals are so active that they do not exist as elements when in contact with air or water. None of the elements in group IA or IIA exist in nature as elements. All the alkali elements exist in natural compounds as unipositive ions; all the alkaline earth elements exist as dipositive ions.

**Metallic Character.** Chemically, the metallic character of an element is associated with the tendency to lose electrons. The metallic character in A families tends to increase from top to bottom in the periodic table. This trend is probably less pronounced in the alkali family than in any other. In the great majority of chemical reactions the elements from sodium to cesium act in the same way. Lithium is somewhat apart, probably because its ion is so small that it has an abnormal charge density for a singly charged ion. Lithium is certainly a metal, but it is the least metallic of the group if rated on the basis of its properties as an electron donor. Cesium is the most metallic.

In the alkaline earth family there is also a great similarity between family members as far as chemical properties are concerned. Calcium, strontium, and barium are notably alike; magnesium and beryllium differ from these three by being somewhat less active. This can be related to the higher ionization energies of the latter two. Also, their ions are very small and have high charge densities; beryllium even tends to form some covalent bonds.

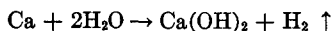
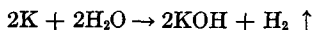
All the alkaline earth elements are metals, beryllium being the least active electron donor and barium the most active.

**Characteristic Reactions.** The alkali and alkaline earth metals are powerful reducing agents, because they lose electrons so readily. They

**METALS: CHEMICAL PROPERTIES  
AND COMPOUNDS**

combine energetically with most nonmetal elements, forming ionic compounds, such as halides, hydrides, oxides, and sulfides. Because lithium and the alkaline earth metals react directly with nitrogen at high temperatures, they continue to burn in air even after they have combined with all the oxygen available.

The alkali metals react spectacularly with water; calcium, strontium, and barium react less violently. Sample reactions are:



In the case of potassium, rubidium, and cesium the reactions are so rapid and so exothermic that the hydrogen evolved usually bursts into flame. Lithium reacts much more slowly than the other group IA elements but still rapidly enough so that the lithium-water reaction has been studied for use as a propellant reaction for torpedoes. Of the elements in IIA, beryllium and magnesium do not react appreciably with water at room temperature.

All the elements tarnish quickly in air, and all except beryllium and magnesium corrode steadily till they are completely converted into oxides or hydroxides or carbonates. Beryllium and magnesium oxidize readily, but the tough oxide film that is formed tends to protect the underlying metal from further attack at room temperature. When strongly heated, even these two metals burn violently. At high temperatures magnesium reacts with nitrogen or carbon dioxide.

Lithium is similar to magnesium in many chemical reactions, and beryllium is similar to aluminum. This diagonal relationship of similarities involving a period 2 element and a period 3 element in the next group shows up in other instances also. For instance, we shall see that boron is similar to silicon.

The principal chemical reactions of the elements in groups IA and IIA are listed in Tables 19-3 and 19-4. It is evident from these data that the elements in these two groups have many common chemical characteristics. Their reactions with oxygen, sulfur, the halogens, hydrogen, water, and the hydrogen ion follow the same pattern. Later in the chapter we shall find that they form similar compounds with most negative ions.

**TABLE 19-3**     *Reactions of group IA metals (M represents an alkali metal)*

$4\text{M} + \text{O}_2 \rightarrow 2\text{M}_2\text{O}$	limited amount of $\text{O}_2$
$2\text{M} + \text{O}_2 \rightarrow \text{M}_2\text{O}_2$	heated in air
$2\text{M} + \text{X}_2 \rightarrow 2\text{MX}$	$\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{or I}$
$2\text{M} + \text{S} \rightarrow \text{M}_2\text{S}$	Se and Te also react
$2\text{M} + 2\text{H}_2\text{O} \rightarrow 2\text{MOH} + \text{H}_2$	violent, except with Li
$2\text{M} + 2\text{NH}_3 \rightarrow 2\text{MNH}_2 + \text{H}_2$	with catalyst
$2\text{M} + \text{H}_2 \rightarrow 2\text{MH}$	dry $\text{H}_2$ gas
$2\text{M} + 2\text{H}^+ \rightarrow 2\text{M}^+ + \text{H}_2$	violent

*Reactions of group IIA metals (M represents an alkaline earth metal)*

TABLE 19-4

$2M + O_2 \rightarrow 2MO$	Be and Mg must be heated
$M + O_2 \rightarrow MO_2$	Ba, Sr; high oxygen pressure helps
$M + X_2 \rightarrow MX_2$	X = F, Cl, Br, or I
$M + S \rightarrow MS$	Se and Te also react
$M + 2H_2O \rightarrow M(OH)_2 + H_2$	Mg and Be react only with steam to give oxides
$3M + N_2 \rightarrow M_3N_2$	heated
$M + H_2 \rightarrow MH_2$	heated; Be and Mg do not react
$M + 2H^+ \rightarrow M^{2+} + H_2$	rapid

COMPOUNDS OF IA AND IIA ELEMENTS

**General Considerations.** Because of the striking chemical similarity of the alkali metals, their compounds tend to be so much alike that we really need to discuss only the sodium and potassium compounds. Sodium compounds are most widely used, because they are cheapest.

The chemical differences between the various alkali ions are so slight that one can be substituted for another in most laboratory and industrial reactions. In some cases, however, substitution of one ion for another is not desirable. For instance, plants must secure potassium from the soil for proper growth, and hence fertilizers must contain potassium compounds; sodium compounds cannot be used for this purpose.

All the alkali ions are colorless and quite inactive. Their simple salts—such as LiCl, KNO<sub>3</sub>, Cs<sub>2</sub>SO<sub>4</sub>, and Rb<sub>2</sub>CO<sub>3</sub>—are usually very soluble in water. Solutions of these compounds are typically strong electrolytes. Lithium compounds resemble magnesium compounds; for example, the solubilities of their carbonates and phosphates are low.

Among the alkaline earths, calcium, strontium, and barium form compounds that are very similar to one another. Magnesium, and more particularly beryllium, form compounds that differ from the other three in properties. Because of its small ionic size (hence, a large charge density), beryllium forms covalent-ionic and covalent bonds with a number of other atoms.

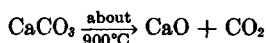
The compounds of beryllium tend to hydrolyze in water, partly because of the formation of the insoluble hydroxide, Be(OH)<sub>2</sub>. The high charge density of the tiny Be<sup>2+</sup> ion enables it to attack water; in this and in some other ways it resembles the Al<sup>3+</sup> ion.

The ions of the alkaline earth elements are colorless and fairly inactive. Many of their simple salts—such as MgSO<sub>4</sub>, CaCl<sub>2</sub>, Ba(NO<sub>3</sub>)<sub>2</sub>, and BeSO<sub>4</sub>—are very soluble. However, the sulfates, normal carbonates, and normal phosphates of calcium, strontium, and barium are only slightly soluble.

**Oxides.** The group IA oxides of the  $M_2O$  type ( $Na_2O$ ,  $K_2O$ , etc.) are white solids that are extremely sensitive to moisture and carbon dioxide, reacting to form the hydroxides,  $MOH$ , and the carbonates,  $M_2CO_3$ , respectively.

The monoxides of the alkali metals can be obtained by heating the metals in a limited supply of dry air at relatively low temperatures (below about  $180^\circ C$ ).

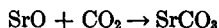
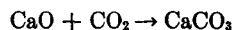
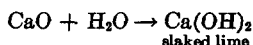
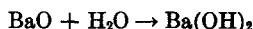
The common oxides of group IIA have the expected formula,  $MO$ . Both lime,  $CaO$ , and magnesia,  $MgO$ , are made by the high-temperature decomposition of naturally occurring carbonate rocks in *lime kilns*. The reaction for lime is



Magnesia is used for firebrick and as insulation for steam pipes. Lime is used to make mortar and plaster and to neutralize acid soils; it also is the cheapest industrial source of hydroxide ions (slaked lime).

Its extreme affinity for water makes calcium oxide widely used for the dehydration of such liquids as alcohol, and for the drying of gases.

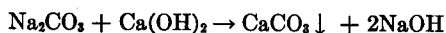
The group IIA oxides are white solids with very high melting points. They tend to react slowly with the water and carbon dioxide in the air to form the hydroxide and the carbonate, respectively:



The reaction with water is an exothermic process called **slaking**. In the case of barium oxide the heat of slaking is so great that, if only a little water is used, the mass may become visibly red hot. When slaked lime is used in a mortar in laying bricks, the setting process involves drying and crystallization, followed by the slow conversion of the slaked lime to calcium carbonate by the action of carbon dioxide from the atmosphere.

The more active alkali and alkaline earth metals form peroxides that are useful oxidizing agents. Sodium peroxide,  $Na_2O_2$ , potassium peroxide,  $K_2O_2$ , and barium peroxide,  $BaO_2$ , are well-known examples. Sodium peroxide is formed when sodium is burned in a stream of dry oxygen; barium peroxide is formed when barium oxide is heated in air. These two peroxides are sometimes used as a source of oxygen and of hydrogen peroxide (see Chap. 6). Superoxides and ozonides, such as  $KO_2$  and  $KO_3$ , are being studied as possible *air revitalizers* for manned satellites and rockets. Not only can they be decomposed to yield oxygen for breathing, but the simple oxides produced can then be used to remove exhaled carbon dioxide from the air. First,  $4KO_2(s) \rightarrow 2K_2O(s) + 3O_2(g)$ ; then  $K_2O(s) + CO_2(g) \rightarrow K_2CO_3(s)$ .

**Hydroxides.** Two of the most widely used strong bases are sodium hydroxide and calcium hydroxide. Because of its lower solubility, calcium hydroxide does not form a concentrated solution, but it is a typical strong base. The equations for preparing calcium hydroxide were given in the preceding section. About one-fifth of the sodium hydroxide (lye) used in this country is made by a process in which calcium hydroxide is a raw material:



Of the four possible compounds, calcium carbonate is the least soluble, so that it precipitates from the concentrated solution, leaving the sodium hydroxide in solution.

Sodium hydroxide is made in huge quantities by the electrolysis of sodium chloride brine (see Figs. 21-4 and 21-5). This process is the cheapest source of *concentrated* hydroxide solutions for the chemical industry. Sodium hydroxide is used in the production of soap, petroleum, rayon, textiles, and paper pulp.

Large quantities of calcium hydroxide are used in the manufacture of mortar, bleaching powder, and ammonia (see Chap. 23) and in water softening.

Magnesium hydroxide is the familiar *milk of magnesia*, the anti-acid slurry long used as a household remedy.

**Halides.** A number of the alkali and alkaline earth halides occur so abundantly in nature that they serve as the raw material for making other compounds of the metals and halogens. Sodium chloride and potassium chloride are mined directly. During the purification of their ores or solutions, other halides—such as lithium, rubidium, and cesium chlorides, and some bromides and iodides—that are present to a small extent in the ores are recovered. Most of the potassium chloride thus obtained, about 3 million tons annually in the United States, is used in fertilizers.

Magnesium chloride is produced from salt wells and from sea water, as one step in the production of elemental magnesium. Calcium chloride, found in nature, is produced synthetically on a large scale as a by-product of the Solvay process for making sodium carbonate. Used as a drying agent, it is also put on dusty roads because of its tendency to *deliquesce*, that is, to remove moisture from the air and form droplets of concentrated solution.

**Carbonates.** The alkali carbonates,  $\text{M}_2\text{CO}_3$ , are much more soluble than the alkaline earth carbonates,  $\text{MCO}_3$ , a fact that explains why the latter are more commonly found as beds of sedimentary rock. Carbonates are among the most abundant natural group IIA compounds. Calcium carbonate is deposited on the ocean floor as the lowly oyster shell, as lacy coral, or in other forms. Geological meta-



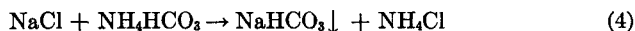
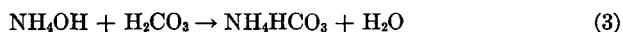
morphosis then produces great beds of limestone, or marble, or even beautifully transparent, colorless crystals of calcite. Though their appearances differ, all these forms are essentially  $\text{CaCO}_3$ . Magnesium carbonate, calcium carbonate, calcium bicarbonate, and sodium bicarbonate are discussed in Chap. 24.

Of all the alkali compounds, sodium carbonate,  $\text{Na}_2\text{CO}_3$ , is second only to sodium chloride in terms of tons used, almost 6 million tons annually in the United States. It is a strong base and a source of carbonate ions for the chemical industry. Large amounts are used in making glass, soap, and paper and in cleaning preparations (washing soda) and water softeners. Although produced commercially from natural salt lakes, the demand for sodium carbonate is so great that about 90 per cent of it is made from  $\text{NaCl}$  and  $\text{CaCO}_3$ .

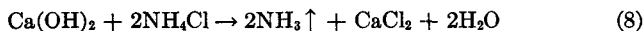
**SOLVAY PROCESS.** Sodium carbonate cannot be made directly from  $\text{NaCl}$  and  $\text{CaCO}_3$ , the cheapest  $\text{Na}^+$  and  $\text{CO}_3^{2-}$  compounds found in nature. When these two substances are mixed in a water solution, nothing happens, because the calcium carbonate is too insoluble:



But starting with these two raw materials, an indirect process was developed almost 200 years ago by Ernest Solvay, a Belgian chemist. The series of reactions involved in the Solvay process may be summarized as follows:



Auxiliary reactions:



As far as the preparation of  $\text{Na}_2\text{CO}_3$  is concerned, the key reaction in the series above is (4). Of the four compounds involved there, sodium bicarbonate is the least soluble. When ammonium bicarbonate is added to a solution saturated with sodium chloride, sodium bicarbonate precipitates. If conditions are carefully controlled, no  $\text{NH}_4\text{Cl}$  will precipitate.

From the viewpoint of economy of the process, the key reaction is (8). The most expensive compound in the whole series of reactions is ammonia, which is left in solution as  $\text{NH}_4^+$  ion ( $\text{NH}_4\text{Cl}$ ) in reaction (4). Indeed, the ammonia left in solution is about as valuable as the  $\text{NaHCO}_3$  precipitated; hence the  $\text{NH}_3$  must be carefully recovered and used over and over. In (8), the recovery reaction, advantage is

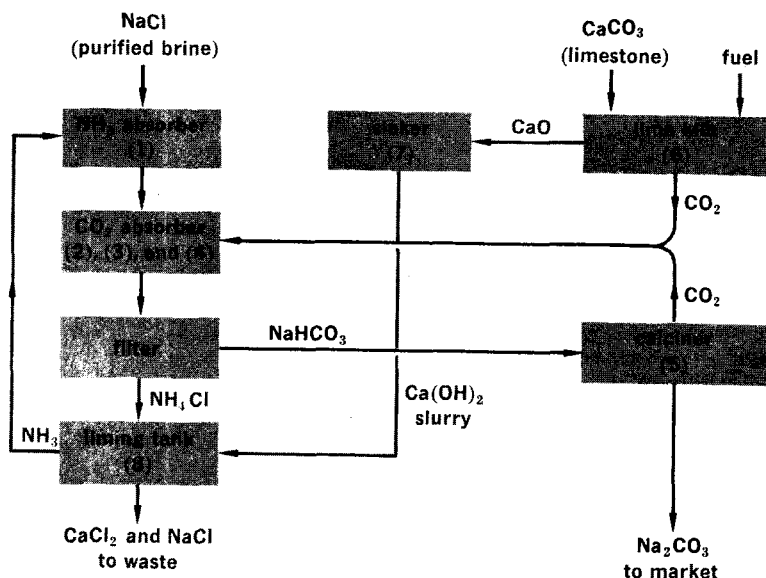
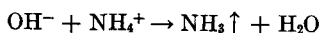


FIG. 19-2

A flow sheet showing the major steps in the Solvay process.

taken of the fact that a strong base liberates  $\text{NH}_3$  from a solution containing  $\text{NH}_4^+$  ions:



The ammonia recovered is pumped back to the first tank and used in reaction (1) again. When all the operations are going well, only 2 to 3 lb of ammonia is lost per ton of sodium bicarbonate produced. Small quantities must be added at intervals to hold the total amount of ammonia fairly constant.

The only raw materials needed in the overall process are fuel, sodium chloride, and calcium carbonate (limestone). The product is sodium carbonate. The by-products, calcium chloride and unused sodium chloride in solution, are usually discarded, because there is no market for them. In some localities there is a market for the calcium chloride.

A flow diagram of the Solvay process is shown in Fig. 19-2. The numbers in it refer to the eight reactions written to summarize the process.

Sodium carbonate is one of the cheapest very soluble bases used by industry. In the accompanying tabulation, its approximate cost is compared with the cost of some other bases in terms of cost per ton and cost per ton-equivalent weight:

		per ton	per ton-equiv. wt
limestone	$\text{CaCO}_3$	\$ 4	\$ 200
lime	$\text{CaO}$	14	390
soda ash	$\text{Na}_2\text{CO}_3$	30	1,600
caustic soda	$\text{NaOH}$	75	3,000
(aqua) ammonia	$\text{NH}_3$	70	1,200

## METALS: CHEMICAL PROPERTIES AND COMPOUNDS

**Sulfates.** Sodium sulfate,  $\text{Na}_2\text{SO}_4$ , is used in making glass and in one process for pulping wood. Potassium sulfate,  $\text{K}_2\text{SO}_4$ , is a desirable ingredient of certain types of fertilizer.

The solubility of the alkaline earth sulfates decreases markedly, from the very soluble beryllium sulfate to the practically insoluble barium sulfate. It is common in chemical analysis to add soluble barium chloride to a sulfate-containing solution and then collect and carefully weigh the barium sulfate precipitate. From the weight of the barium sulfate can be calculated the weight of the sulfate in the original solution.

Magnesium sulfate,  $\text{MgSO}_4$ , and calcium sulfate,  $\text{CaSO}_4$ , are mentioned in Chap. 22.

**Other Compounds.** The elements of groups IA and IIA form stable compounds with practically all the known negative ions. Their exceptional solubility in water and their low cost make the sodium compounds the most widely used sources of specific anions for chemical reactions.

Because of their low electronegativities, these elements (except beryllium and magnesium) react at high temperatures with hydrogen to form saltlike compounds. Some of these hydrides can be melted and electrolyzed, the metal ion going to the negative pole, and the hydride ion,  $\text{H}^-$ , going to the positive pole. In such compounds hydrogen behaves like a halogen.

## TRANSITION METALS AND THEIR NEIGHBORS

In the remainder of this chapter we take up all the transition metals and some of their neighbors—about 65 elements in all; this includes all the metals not heretofore discussed. We are not able to devote much attention to each one, but we describe some of their important physical and chemical properties and point out some important similarities and differences in the elements.

### CLASSIFICATION

On the basis of their position in the periodic table, the metals under discussion are often grouped into families as follows:

**Transition and Inner Transition Metals.** The *scandium family*: scandium, Sc, yttrium, Y, lanthanum, La (and the lanthanide series), and actinium, Ac (and the actinide series).

The *titanium family*: titanium, Ti, zirconium, Zr, and hafnium, Hf.

The *vanadium family*: vanadium, V, niobium, Nb, and tantalum, Ta.

The *chromium family*: chromium, Cr, molybdenum, Mo, and tungsten, W.

The *manganese family*: manganese, Mn, technetium, Tc, and rhenium, Re.

The *iron family*: iron, Fe, cobalt, Co, and nickel, Ni.

The *platinum family*: ruthenium, Ru, rhodium, Rh, palladium, Pd, osmium, Os, iridium, Ir, and platinum, Pt.

*Neighbors of Transition Metals.* The *copper family*: copper, Cu, silver, Ag, and gold, Au.

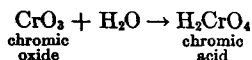
The *zinc family*: zinc, Zn, cadmium, Cd, and mercury, Hg.

The *aluminum family*: aluminum, Al, gallium, Ga, indium, In, and thallium, Tl.

The *germanium family*: germanium, Ge, tin, Sn, and lead, Pb.

Antimony, Sb, and bismuth, Bi, although metallic in character, are included in the nitrogen family (Chap. 23), and polonium, Po, is classified in the sulfur family (Chap. 22).

*Metallo-Acid Elements.* The titanium, vanadium, chromium, and manganese families have several common characteristics, one of which is that they form metallic oxides that are acidic:



By grouping similar metals together we can simplify this discussion, so we shall use the term *metallo-acid elements*, a name based on their acid-forming nature, to refer to the 12 metals in these 4 families.

## PHYSICAL PROPERTIES

The transition elements and their neighbors exhibit typical metallic properties. In general, they are *malleable* (Fig. 17-21), *ductile*, and *good conductors of heat and electricity*, and they show a *metallic luster*.

The structures of these metals are of the close-packed types. The atoms are stacked like balls into a body-centered, or face-centered, or hexagonal close-packed structure (see Fig. 17-18). Except for copper and gold, which have characteristic colors, all 65 metals are similar in appearance, resembling tin or iron to some extent.

### *Physical properties of elements of first transition series*

**TABLE 19-5**

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
electron configuration	2,8,9,2	2,8,10,2	2,8,11,2	2,8,13,1	2,8,13,2	2,8,14,2	2,8,15,2	2,8,16,2
density, g/ml	3.1	4.43	6.07	7.19	7.21	7.87	8.70	8.90
melting point, °C	1400	1812	1730	1900	1244	1535	1493	1455
boiling point, °C	3900	3277	3377	2642	2087	2800	3100	2800
covalent radius, Å	1.44	1.32	1.22	1.17	1.17	1.16	1.16	1.15
ionization energy, volts	6.56	6.83	6.74	6.76	7.43	7.90	7.86	7.63
electronegativity	1.3	1.6	1.7	1.6	1.5	1.7	1.7	1.8

The properties of the elements in the first transition series are summarized in Table 19-5. A number of trends that are obvious in this table are typical of transition elements:

1. The number of electrons in the outside energy level tends to remain constant (although there is some variation).

**METALS: CHEMICAL PROPERTIES  
AND COMPOUNDS**

2. The melting and boiling points are uniformly high but do not vary in a regular way.

3. The covalent radius of the atoms is remarkably constant. In the second and third series these values increase slightly, starting at rhodium, Rh, and iridium, Ir, respectively. But even in these cases the main point is that these radii are very nearly the same (see Fig. 19-1).

4. The ionization energy tends to increase slightly as the positive charge on the nucleus (atomic number) increases.

These four points reveal strong "horizontal similarities" between adjacent transition elements.

There are even greater similarities among the members of the first inner transition series, the lanthanides. Some of the lanthanides, especially the adjacent ones, are so nearly identical in chemical and physical properties that it is difficult to tell their compounds apart. It is extremely tedious to separate the individual elements from the mixtures of compounds found in nature, because they react in similar ways to all ordinary physical or chemical forces. Undoubtedly this similarity is due to the presence of the same number of electrons in both the outside and the first inner energy levels.

**TABLE 19-6**      *Second transition series*

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
density, g/ml	5.5	6.24	8.57	10.2		12.2	12.5	12
melting point, °C	1500	1852	2487	2610	2200	2500	1960	1550
boiling point, °C	3230	3578	(5130)	5560		4110	3960	3560

*Third transition series*

	La	Hf	Ta	W	Re	Os	Ir	Pt
density, g/ml	6.2	13.3	16.6	19.3	21.0	22.6	22.5	21.5
melting point, °C	920	2215	2996	3380	3180	2700	2443	1770
boiling point, °C	4242	5230	5430	5680	5630	4400	4350	3830

Table 19-6 shows the melting points, boiling points, and densities for the second and third transition series. A comparison of Tables 19-5 and 19-6 reveals the same general trends for the second and third series as those noted above for the first series. However, the melting points and densities of the second transition series are generally higher than those for corresponding members of the first series; those for the third series are the highest of all. For example, osmium, iridium, and platinum in the third series have the greatest densities of all elements—or, for that matter, of all known substances. Tungsten and rhenium in the same series have the highest boiling points of all the elements. Their melting points are exceeded only by that of carbon.

*Neighbors of transition elements*

TABLE 19-7

	electrons	density, g/ml	melting point, °C	boiling point, °C
family IB:				
copper	2,8,18,1	8.9	1087	2582
silver	2,8,18,18,1	10.5	961	2193
gold	2,8,18,32,18,1	19.3	1063	2710
family IIB:				
zinc	2,8,18,2	7.1	420	907
cadmium	2,8,18,18,2	8.6	321	767
mercury	2,8,18,32,18,2	13.6	-39	357
family IIIA:				
aluminum	2,8,3	2.7	660	2327
gallium	2,8,18,3	5.9	30	1983
indium	2,8,18,18,3	7.3	157	2000
thallium	2,8,18,32,18,3	11.8	304	1457
family IVA:				
germanium	2,8,18,4	5.3	960	2830
tin	2,8,18,18,4	7.3	232	2340
lead	2,8,18,32,18,4	11.3	328	1744

Table 19-7 shows certain properties of the neighbors of the transition metals. The densities here range from that of the light metal, aluminum (2.7), to that of one of the denser metals, gold (19.3). The melting points range from those of the lowest melting metals, mercury and gallium, to those of metals with intermediate values, copper, silver, and gold.

**CHEMICAL PROPERTIES**

**Chemical Activity.** The general activity of the metals in the middle of the periodic table varies greatly but is always less than that of the alkali and alkaline earth metals. For example, aluminum and zinc are quite active, and iron and lead moderately so. However, silver, gold, and the platinum metals are inactive to the point of semi-inertness and so are referred to as *noble metals*. The relative activity of metals can be estimated by comparing their electrode potentials:

1. The group IIIB elements and the members of the lanthanide and actinide series are very active, with oxidation potentials usually below that of sodium (2.71 volts) but above that of aluminum (1.66 volts).

2. The metallo-acid elements are moderately active, with oxidation potentials usually below aluminum (1.66 volts) but above hydrogen (0.00 volt).

3. The three members of the iron family are also moderately active. Comparable values of oxidation potentials are iron (0.44 volt), cobalt (0.28), and nickel (0.25).

4. The platinum metals are chiefly notable for their chemical inactivity, and their oxidation potentials are in line with this behavior.

All are below copper in the activity series, with oxidation potentials ranging from ruthenium ( $-0.45$  volt) down to iridium ( $-1.15$  volts).

5. The neighbors of the transition metals range widely in activity from aluminum to gold. A number of them are listed in Table 18-1: aluminum (1.66 volts), zinc, tin, lead, copper, mercury, silver, and gold ( $-1.50$  volts).

**Corrosion.** Closely related to the chemical activity of the metals is the phenomenon of **corrosion**, the chemical attack on a metal by its environment. The most common type of corrosion is due to the action of the atmosphere in conjunction with water and various substances dissolved in the water. Essentially, corrosion is a reaction in which a metal is oxidized. In most cases the reaction is definitely electrochemical in nature and involves the type of electron transfer that is characteristic of voltaic cells (batteries).

Moisture is necessary for the atmospheric corrosion of all but the most active metals. If salts are dissolved in the moisture, the corrosion is speeded up, presumably because a solution of electrolytes is an ideal medium for electrochemical oxidation-reduction. The presence of any substance that dissolves and forms an acid solution—for example, sulfur dioxide or carbon dioxide—usually increases the rate of corrosion. Oxygen that is dissolved in water is an important corrosion agent.

In general, metals high in the electrochemical series, that is, those which have large positive oxidation potentials, corrode easily. In this category are the group IIIB elements and the lanthanides (and also the alkali and alkaline earths, which corrode rapidly even in dry air). Metals low in the series—the noble metals—do not corrode easily.

The position of a metal in the electrochemical series is not the only factor that determines the extent or rate of corrosion. Just as important is the type of film or coating that is formed on the surface of the metal. Aluminum and magnesium actually react quickly when exposed to air; but the thin, closely packed film of oxide that forms on the surface protects the underlying metal from further corrosion. These two metals corrode less completely in air than the less active metal, iron. The rust formed on the surface of iron is so flaky and porous that the corroding chemicals can pass through it easily and attack the underlying metal.

The formation of a protective film explains the paradox of galvanized iron. Iron is protected from corrosion by being coated with the more active metal, zinc. Zinc reacts readily with moisture, oxygen, and carbon dioxide, but it forms a tough film of basic carbonate,  $\text{Zn}(\text{OH})_2 \cdot \text{ZnCO}_3$ , that resists further attack.

The rusting of underground pipes may necessitate costly repairs or even replacement. One ingenious method of preventing corrosion of iron pipes is *cathodic protection*. Pieces of an active metal, such as magnesium, are buried in the ground near the pipe and connected to

Cathodic protection of an underground pipeline.

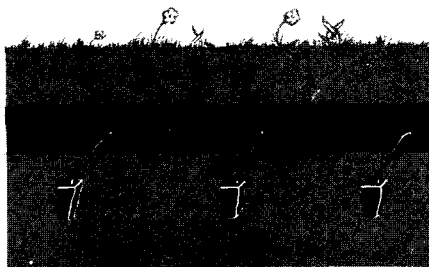


FIG. 19-3

it by a wire. Instead of the iron losing its own electrons directly to the oxidizing agents (corrosion agents) that attack it, it merely relays, via the wire, electrons from the more active metal. The slug of active metal corrodes away, but the costly pipe line is protected. A cathodic protection system is diagramed in Fig. 19-3.

**Oxidation States.** A noteworthy characteristic of the transition metals and their neighbors is that most of them tend to show several oxidation states. This is in contrast to the alkali and alkaline earth metals (groups IA and IIA), which form cations only of +1 and +2 charge, respectively. The most common oxidation states for the members of the first transition series (Sc through Ni) are indicated in Fig. 5-1. There are many possible oxidation states not indicated; for instance, the +6 state of iron, or the +2, +3, and +4 states of vanadium.

Some important generalizations applicable to all three transition series can be made. Reference to Fig. 5-1 will show how these apply to the first series.

1. None of these elements has a common oxidation state of less than +2.

2. Each of the elements in groups IIIB to VIIB can exhibit the appropriate maximum oxidation state for its group. Examples of compounds include titanium dioxide,  $\text{TiO}_2$ , chromium trioxide,  $\text{CrO}_3$ , and rhenium heptoxide,  $\text{Re}_2\text{O}_7$ .

3. Most of the elements in group VIIIB have +4 as their maximum oxidation state. But two of the nine elements have an oxidation state of +8, the highest shown by any element (osmium oxide is  $\text{OsO}_4$ ).

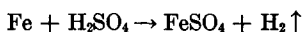
By a suitable choice of oxidizing agents and of concentration and temperature, an element can be made to assume any of its possible oxidation states. We must emphasize that for oxidation states of +4 and over, the ions are not simple. Indeed, no discrete ions may be formed; rather, the small highly charged particle will form covalent bonds with other molecules or ions if they are available. Examples include osmium oxide,  $\text{OsO}_4$ , wherein the osmium has a calculated state of +8, even though the  $\text{Os}^{8+}$  ion does not exist as a separate



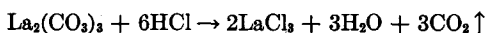
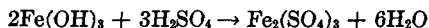
particle. A similar case is potassium dichromate,  $K_2Cr_2O_7$ , in which chromium has a calculated state of +6.

**Binary Compounds and Simple Salts.** Practically all the metals form compounds with well-known anions, such as halide, nitrate, acetate, sulfate, oxide, carbonate, hydroxide, phosphate, sulfide, and silicate. The first four anions tend to form water-soluble compounds, the latter six to form insoluble compounds. In all these compounds the metal is in a positive oxidation state. Most of the transition metals form more than one salt.

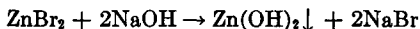
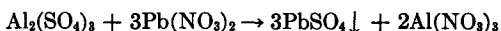
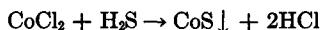
If the desired compounds are not found in nature, they can be prepared easily. For example, salts can be formed in a variety of ways, as by allowing a metal to react with an acid:



Another way is to allow a hydroxide or a carbonate to react with an acid:



In water solution, such salts undergo partner exchange reactions (metathesis), depending on the relative solubilities of the compounds:



Precipitation reactions similar to these are often used to prepare a compound, to remove a certain ion from a solution, or to analyze materials.

**Color of Compounds.** One of the most characteristic properties of compounds is their color. Color is not a trivial property, but, as we saw in Chap. 17, is related to the electronic structures of the molecules or ions present in the compound.

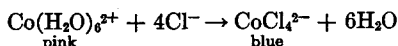
The transition elements are noted for the fact that they form colored compounds. This behavior is often associated with the excitation of *d* electrons in partially filled sublevels. Radiation in the visible range, between 1.8 and 3.1 eV/photon, is of the proper energy to excite *d* electrons to higher energy levels. Another factor related to color is the coexistence of two oxidation states of an element. Some of the most intensely colored materials are those containing different ions of the same element. Blueprint dye, for example, contains  $Fe^{2+}$  and  $Fe^{3+}$  in complex ions. Having ions that can easily exchange electrons evidently increases the number of electronic excitations that absorb wavelengths of visible radiation.

*Colors of ions in dilute water solutions*

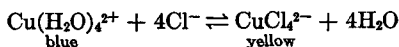
TABLE 19-8

colorless	Na <sup>+</sup> , Mg <sup>2+</sup> , Sc <sup>3+</sup> , Ti <sup>4+</sup> , Cu <sup>+</sup> , Zn <sup>2+</sup> , Al <sup>3+</sup>
pink	Co <sup>2+</sup> , Mn <sup>2+</sup>
yellow	Fe <sup>3+</sup> , CrO <sub>4</sub> <sup>2-</sup> , Au <sup>3+</sup> , Au <sup>+</sup>
green	Fe <sup>2+</sup> , V <sup>3+</sup> , Ni <sup>2+</sup>
blue	Cr <sup>2+</sup> , Cu <sup>2+</sup>
purple	MnO <sub>4</sub> <sup>-</sup> , Ti <sup>3+</sup>
violet	Mn <sup>3+</sup> , Cr <sup>3+</sup> , V <sup>2+</sup>

The colors of some of the ions of the transition elements and other elements are listed in Table 19-8. Note that the color is often different for different oxidation states of the same element. The color is also modified by the formation of hydrates, ammoniates, and other complex ions. An interesting example is afforded by Co<sup>2+</sup> complex ions. A dilute aqueous solution of cobalt(II) chloride has the pale pink color characteristic of the complex ion Co(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>. This solution is sometimes used as an "invisible" ink. Upon warming, the writing becomes visible because of the formation of anhydrous CoCl<sub>2</sub>, which is deep blue. The addition of considerable hydrochloric acid to pink cobalt chloride solutions changes the color to blue because of the formation of the complex chloride, CoCl<sub>4</sub><sup>2-</sup>:



Another common example involves Cu<sup>2+</sup>. Anhydrous copper sulfate, CuSO<sub>4</sub>, is colorless. When it is dissolved in water, the characteristic blue color of hydrated copper ions, Cu(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>, appears. If excess chloride ions (from HCl or other very soluble chlorides) are dissolved in the solution, the color becomes green. The green color is attributed to an equilibrium mixture of blue and yellow ions:



## COORDINATION COMPOUNDS

Metals form practically all the simple compounds with nonmetals that we expect, with the metals existing in all their varied oxidation states. In addition, many transition metal atoms or ions form molecules or complex ions by combining with ligands via covalent bonds to which the ligands donate both the electrons. Examples are given in Fig. 19-4. Compounds containing such molecules or complex ions are called **coordination compounds**. Elements other than the transition elements can form coordination compounds, particularly if ions of these elements have high charge densities, for example, Be<sup>2+</sup> and Mg<sup>2+</sup>.

The reaction that produces the coordinated molecule or ion is an example of a Lewis acid-base reaction; the central atom acts as the Lewis acid (electron pair acceptor), and the ligand acts as the base

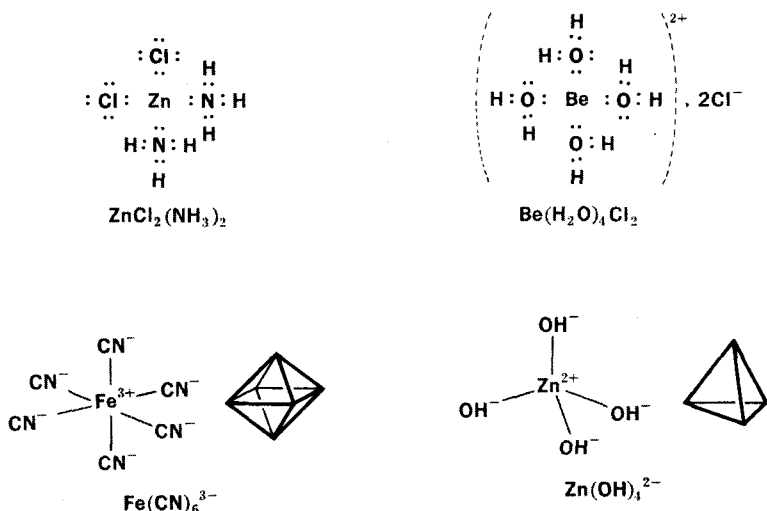


FIG. 19-4

Examples of complex compounds and ions. In the first two instances, the electrons formally associated with the ligand (electron-donor atom) are shown as colored dots. In the latter two instances, ligand-electron pairs are denoted by lines and the overall geometry of the complex is shown in color.

(electron pair donor). The ligand may be an atom, ion, or molecule having a pair of unshared electrons that it can donate. Commonly, the element in the ligand that has an electron pair to donate is oxygen, sulfur, or nitrogen. The central atom or ion that accepts the electron pair must have vacant orbitals of relatively low energy available for bonding.

In the case of coordination compounds of the transition elements, *d* orbitals are usually involved in the bonding. Available *d* orbitals join with *s* and *p* orbitals of comparable energy to form *hybrid orbitals*. Some general examples of hybridization were described in Table 17-2; a few more specific examples are shown in Table 19-9.

**LABILITY OF LIGANDS.** The cyanide ion,  $\text{CN}^-$ , is an example of a ligand that is usually strongly held in a coordination compound. Although a solution of KCN is extremely poisonous, owing to free  $\text{CN}^-$  ions, a solution of an ion, such as  $[\text{Fe}(\text{CN})_6]^{3-}$ , is relatively harmless, because the  $\text{CN}^-$  ligands are so strongly bound to the central atom. If a ligand in a complex ion is not strongly held, it is said to be *labile*, or free to move. In a water solution of  $\text{Fe}^{3+}$  and  $\text{Cl}^-$  ions, the complex  $[\text{Fe}(\text{Cl})_6]^{3-}$  might be expected to form. However, the  $\text{Cl}^-$  ion is a labile ligand that can exchange places in aqueous solution with a labile  $\text{H}_2\text{O}$  ligand. Complexes such as  $[\text{FeCl}_2(\text{H}_2\text{O})_4]^+$  and  $[\text{FeCl}_3(\text{H}_2\text{O})_3]$  exist, with the proportions of chloride ion and water molecules in the complexes depending on the concentration of chloride ion in solution.

**Isomers.** A number of interesting structures are exhibited by coordination compounds. For instance, two obviously different sub-

## Hybrid orbitals in coordination compounds

TABLE 19-9

simple ion or complex	electrons of ion or central atom (arrows) and electrons of ligands (dots)	information from magnetic measurements	geometry of complex
	$3d$ $4s$ $4p$		
$\text{Fe}^{2+}$		paramagnetic (four unpaired electrons)	
$\text{Fe}(\text{CN})_6^{4-}$ $d^2sp^3$		diamagnetic (no unpaired electrons)	octahedral
$\text{Fe}^{3+}$		paramagnetic (five unpaired electrons)	
$\text{Fe}(\text{CN})_6^{3-}$ $d^2sp^3$		paramagnetic (one unpaired electron)	octahedral
$\text{Co}^{3+}$		paramagnetic (four unpaired electrons)	
$\text{Co}(\text{CN})_6^{3-}$ $d^2sp^3$		diamagnetic (no unpaired electrons)	octahedral
$\text{Ni}^{2+}$		paramagnetic (two unpaired electrons)	
$\text{Ni}(\text{CN})_4^{2-}$ $dsp^2$		diamagnetic (no unpaired electrons)	square planar

stances, one green and the other violet, have the same formula  $\text{Co}(\text{NH}_3)_4\text{Cl}_2$ . By measurement of the electrical conductivity of solutions or by freezing-point depression measurements, both substances have been shown to ionize in solution to yield  $[\text{CoCl}_2(\text{NH}_3)_4]^+$  and  $\text{Cl}^-$  ions. Both the green positive ion and the violet positive ion are octahedral complexes; but in the violet one the two chloride ligands are on the same side (*cis* form) of the octahedron, whereas in the green ion the two chlorides are on opposite sides (*trans* form) of the octahedron.

Molecules or ions that have the same overall composition but different structural formulas are called **isomers**. The *cis* and *trans* isomers of the dichlorotetramminecobalt(III) ion are shown in Fig. 19-5.

**Chelates.** A ligand that has two or more points of attachment to the central atom is called a **chelate** (Greek *chele*, claw). An example of a chelate ligand is the compound  $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ , ethylenediamine. Each nitrogen has a pair of electrons to donate, so that both ends of the molecule can be bound to a central atom. We shall use the symbol (en) for an ethylenediamine molecule in structural formulas.

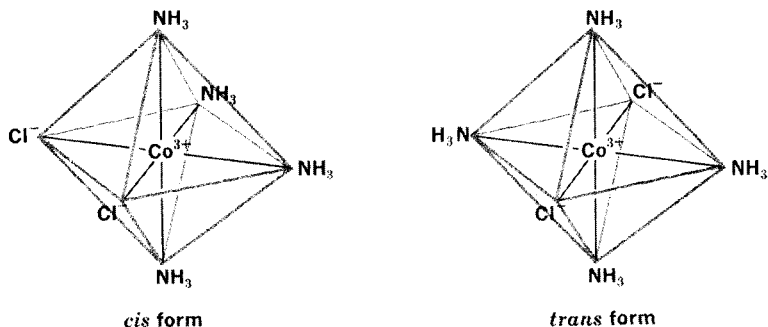
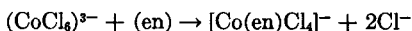


FIG. 19-5

Isomeric forms of dichlorotetramminecobalt(III) ions,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ . The *cis* form is violet, the *trans* form is green.

One ethylenediamine molecule can replace two singly bound ligands, as shown in the reaction with the octahedral  $(\text{CoCl}_6)^{3-}$  ion:



As might be expected, a chelating ligand is held by a central atom more strongly than singly held ligands bound by comparable bonds.

The compound  $[\text{CoCl}_2(\text{en})_2]\text{Cl}$  dissolves to form two ions in solution, one simple  $\text{Cl}^-$  ion and a complex ion  $[\text{CoCl}_2(\text{en})_2]^+$ . The latter has been found to have three possible isomeric forms, as shown in Fig. 19-6. Isomer (a) is called a *trans* form to indicate the positions of

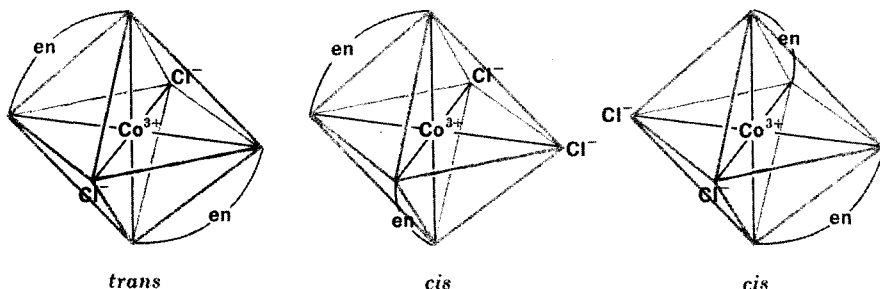


FIG. 19-6

Isomers of dichlorobis(ethylenediamine)cobalt(III) ions. The two *cis* forms are optical isomers.

the two  $\text{Cl}^-$  ligands; isomers (b) and (c) are called *cis* forms. The two *cis* forms may appear to be the same, but there is a subtle difference, which we discuss in Chap. 28, where we take up *optical isomerism*.

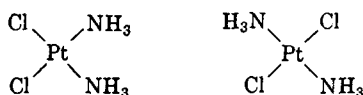
The compound ethylenediamine is called a *bidentate* (two teeth) chelate, because it has two points of attachment to a central atom; there are also *tri-*, *tetra-*, and even *sexadentate* chelates. Two tetradentate compounds of great interest are chlorophyll and heme. There are truly remarkable similarities in structure between these two life-essential compounds, one in the plant and one in the animal kingdom.

## Complex ions

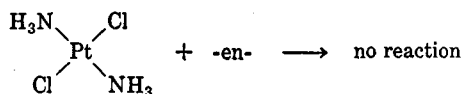
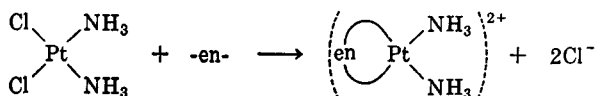
TABLE 19-10

ion	name of ion	representative compound	name of compound
$\text{Fe}(\text{CN})_6^{4-}$	ferrocyanide	$\text{K}_4\text{Fe}(\text{CN})_6$	potassium ferrocyanide
$\text{Fe}(\text{CN})_6^{3-}$	ferricyanide	$\text{Na}_3\text{Fe}(\text{CN})_6$	sodium ferricyanide
$\text{PtCl}_6^{2-}$	chloroplatinate	$\text{H}_2\text{PtCl}_6$	chloroplatinic acid
$\text{Co}(\text{NO}_2)_6^{3-}$	cobaltinitrite	$\text{Na}_3\text{Co}(\text{NO}_2)_6$	sodium cobaltinitrite
$\text{Zn}(\text{OH})_4^{2-}$	zincate	$\text{BaZn}(\text{OH})_4$	barium zincate
$\text{CrO}_4^{2-}$	chromate	$\text{K}_2\text{CrO}_4$	potassium chromate
$\text{Cr}_2\text{O}_7^{2-}$	dichromate	$\text{Na}_2\text{Cr}_2\text{O}_7$	sodium dichromate
$\text{MnO}_4^-$	permanganate	$\text{KMnO}_4$	potassium permanganate
$\text{ReO}_4^-$	perrhenate	$\text{NH}_4\text{ReO}_4$	ammonium perrhenate

In some cases chelate reactions can be used to identify isomers. The compound  $\text{PtCl}_2(\text{NH}_3)_2$  is known to be a square planar complex having *cis* and *trans* isomers:



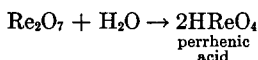
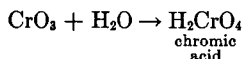
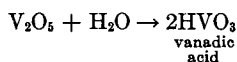
Ethylenediamine will react with the *cis* isomer to replace the two chlorides; but it will not react with the *trans* isomer, evidently because the  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  (-en-) molecule cannot bend up and over the diagonal dimension of the square planar complex:



**Miscellaneous Complex Ions.** The formulas for some commonly encountered complex ions are listed and named in Table 19-10, along with the formulas and names of representative compounds. These ions and ones similar to them are found in many useful compounds. A special word is in order about the four oxy-ions listed last in Table 19-10. The elements in the metallo-acid groups:

Ti	V	Cr	Mn
Zr	Nb	Mo	Tc
Hf	Ta	W	Re

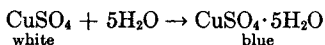
have especially strong tendencies to form stable oxy-anions when in their higher oxidation states. The following shows how their oxides form acids with water, unlike the typical metal oxides, which are basic.



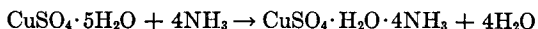
From their formulas it can be seen that these acids are analogous to the more familiar nitric,  $\text{HNO}_3$ , sulfuric,  $\text{H}_2\text{SO}_4$ , and perchloric,  $\text{HClO}_4$ , acids. (See section in Chap. 21 on the naming of oxy-ions.) The existence of *acidic metallic oxides* is explained by the fact that such ions as  $\text{V}^{5+}$ ,  $\text{Cr}^{6+}$ , and  $\text{Re}^{7+}$  are too highly charged to exist as simple ions. Because of their extreme attraction for any negative ions, they form stable negative oxy-anions that then combine with  $\text{H}^+$  ions to form acids. Their oxy-anions have symmetrical shapes, such as tetrahedrons or octahedrons.

**Hydrates and Ammoniates.** Because most reactions are carried out in water solution, the  $\text{H}_2\text{O}$  molecule is often of interest as a ligand. The  $\text{NH}_3$  molecule is a similarly held neutral molecule ligand. In most cases these ligands are labile, but in some compounds they are very tightly held.

Consider the addition of water to anhydrous copper sulfate to form the blue pentahydrate:

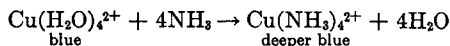


X-ray studies show that there are four water molecules close to each copper ion and that the fifth water molecule is close to a sulfate ion. When ammonia gas is continuously passed over copper sulfate pentahydrate, it is found that only four of the water molecules can be replaced:



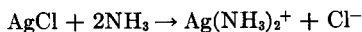
The water molecules attached to the  $\text{Cu}^{2+}$  ion are labile, but the fifth molecule is not.

The cupric ion in water solution actually has the formula  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ . Ammonia can be substituted for water in solution:



This reaction takes place when ammonium hydroxide (ammonia water) is added to water solutions of the cupric ion. The  $\text{Cu}(\text{NH}_3)_4^{2+}$  ion has a deeper blue color than does the hydrated ion.

The dissolving of a silver chloride precipitate by ammonium hydroxide solution is a result of the formation of complex ions. Even though  $\text{AgCl}$  is practically insoluble in pure water, ammonia molecules attach so strongly to  $\text{Ag}^+$  ions that they cause solution to occur.



Although it is common to write  $\text{M}^{x+}$  as a simple formula for a metal ion, in a water solution such an ion often exists as  $\text{M}(\text{H}_2\text{O})_x^{x+}$ , a hydrated ion;  $x$  usually has a value from 2 to 6. Even the metals in groups IA and IIA are hydrated in solution, but they do not tend to form ions with definite numbers of coordinated water molecules so readily as the transition elements do.

The following are representative examples of stable complex ions. Although all of them involve water and ammonia molecules, molecules other than these can also form stable complexes:



Note that in the complex anions described in Table 19-10 the coordinated groups were negative; hence the entire group was negatively charged, for example,  $\text{Zn}(\text{OH})_4^{2-}$ . When the coordinated groups are neutral, a complex cation is formed that has the charge of the central ion, for example,  $\text{Zn}(\text{NH}_3)_4^{2+}$ .

**Uses of Coordination Compounds.** A major use of coordinating and chelating ligands is to influence the available concentration of ions in solution. Phosphate chelating agents are used in water softeners to keep calcium ions in solution; chelated iron is used in fertilizers to provide iron that will not react with soils to form insoluble iron compounds; and chelated metal ions can be formed that are more soluble in oil than in water, the reverse of the usual behavior. New dyes, especially for some of the difficult to tint synthetic fabrics, have been made from coordination compounds.

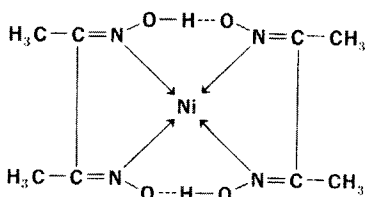
Chelating agents are used to remove unwanted impurities from drinking water. They have also been used in separating the mixtures of metal ions found in the fission products of nuclear reactors.

Not only recent discoveries, but many classical chemical reactions are interpreted today in terms of coordination chemistry. The long-known ability of *aqua regia*, a mixture of concentrated  $\text{HNO}_3$  and  $\text{HCl}$ , to dissolve gold and platinum, depends in large part on the formation of the complex ions  $\text{AuCl}_4^-$  and  $\text{PtCl}_6^{2-}$ , respectively.

The precipitation of the  $\text{Ni}^{2+}$  ion as the brilliant red dimethylglyoxime salt is a classical reaction, used in the laboratory both as a qualitative test for the presence of nickel ion and to remove nickel from solution quantitatively. The fact that dimethylglyoxime combines with nickel ion, but not with iron, cobalt, or most other similar substances, was for long unexplained. Today it is known that the dimethylglyoxime has four points of attachment (tetradentate) and is planar. Thus it nicely satisfies the tendency of nickel to form four  $dsp^2$  hybrid bonds in square planar complexes. Compare Table 19-9



**METALS: CHEMICAL PROPERTIES  
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**FIG. 19-7**

The tetradentate chelate compound nickel dimethylglyoxime. Dotted lines indicate hydrogen bonds.

and see Fig. 19-7. There are many such special compounds formed by the different transition metals.

## **CHAPTER REVIEW**

### *Topics*

Divisions of the periodic table, general properties of metals and non-metals, borderline elements, periodic table and trends in behavior, transition elements, inner transition elements, lanthanide series, actinide series, physical and chemical properties of alkali and alkaline earth metals, compounds of IA and IIA elements, Solvay process, physical and chemical properties of transition metals and their neighbors, color of compounds, coordination compounds, isomers, chelates, complex ions, hybrid orbitals, hydrates and ammoniates.

### *Exercises*

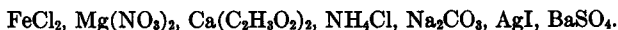
1. a. Using the data early in the chapter for electronegativity ranges for classes such as metals and nonmetals, compare these ranges with Fig. 4-15 and point out some instances in which it is difficult to say to which class an element belongs.  
b. Do the borderline elements divide the periodic table into two distinct areas of differing electronegativities?
2. The freshly broken surfaces of almost all metals have the same luster or "color." Explain what this might mean in terms of absorption and radiation of visible light by metals.
3. "The screening effect does not increase so rapidly as the effect of the nuclear charge in a period." Discuss this first on the basis of the elements magnesium, aluminum, and silicon; then on the basis of calcium, vanadium, and nickel.
4. In periods 5 and 6, at the point at which the  $5p$  and  $6p$  sublevels begin to fill, the atoms increase in size. How might this be accounted for theoretically?
5. How does a ton of magnesium compare in volume with a ton of aluminum; with a ton of iron?
6. There are three main factors that determine how tightly a valence electron is held in an atom. Discuss these factors, using the elements magnesium, calcium, and scandium as examples, and correlate your discussion with ionization energy data.

7.
  - a. It is stated in the text that the electron distributions in the outer two main levels are very nearly constant for the lanthanide and actinide series. Check this statement, and discuss its validity.
  - b. In the light of your discussion, what would you predict about the extent of chemical similarities among the lanthanides as compared with the actinides?
8. On the basis of electron configurations, name for each of the following elements two elements that should be very similar in chemical properties: lutetium, Lu; thorium, Th; europium, Eu; and element 104.
9. From the data on electron configurations inside the front cover, cite evidence that indicates that half-filled *d* and *f* sublevels have a special stability.
10. The metallic structure has been described as positive ions in a sea of electrons (compare Fig. 17-21). What properties of metals justify this description?
11. By means of hypothetical structural diagrams, account for the fact that lithium is harder than cesium, but softer than beryllium.
12. How is the diagonal relationship of similarities between period 2 and 3 elements, for example, Li and Mg, possibly related to the properties of their ions?
13. It is pointed out that one should not handle the alkali metals with bare hands. Write equations for possible reactions and specify the danger to one's skin.
14.
  - a. Using data from Tables 19-1 and 19-2, with any other needed data, calculate the ratio of the experimental densities of sodium-potassium, and compare with the ratio of densities calculated on the basis of atomic radii. Assume similar packing of atoms.
  - b. Repeat for magnesium-calcium.
15. When samples of the alkali metals are heated, each imparts a characteristic color to the flame. When tungsten, or some similar transition metal, is heated sufficiently it becomes white hot. Explain.
16. On the basis of physical properties, explain why rubidium should be intermediate in chemical activity between potassium and cesium.
17. Consider the relative positions of the nine elements in the small square area of the periodic table defined by the atomic numbers 19, 20, 21, 37, 38, 39, 55, 56, and 57. Assuming that the trends in family IIIB are similar to those in IA and IIA, predict:
  - a. Which of the nine elements has the smallest atom; which the largest.
  - b. Which has the smallest electronegativity; which the greatest.
  - c. Which forms the ion with the greatest charge density; which the least.
  - d. Which has the greatest ionization energy; which the least.
  - e. Which would have the greatest metallic character.
  - f. Which would be the most dense.
  - g. Which would have the highest melting point.
  - h. Check your predictions against data tabulated in the text where possible and discuss any discrepancies.

**METALS: CHEMICAL PROPERTIES  
AND COMPOUNDS**

18. Write equations for the following reactions, and state what conditions are necessary for the reactions to occur:
- |  |   |
|--|---|
| a. $\text{Rb} + \text{HOH} \rightarrow$  | f. $\text{K} + \text{S} \rightarrow$            |
| b. $\text{Sr} + \text{O}_2 \rightarrow$  | g. $\text{Ba} + \text{N}_2 \rightarrow$         |
| c. $\text{Be} + \text{O}_2 \rightarrow$  | h. $\text{Li} + \text{NH}_3 \rightarrow$        |
| d. $\text{Mg} + \text{Br}_2 \rightarrow$ | i. $\text{Ca} + \text{H}_2 \rightarrow$         |
| e. $\text{Na} + \text{O}_2 \rightarrow$  | j. $\text{Cs} + \text{H}_2\text{O} \rightarrow$ |
19. Which of the following compounds are water-insoluble:  $\text{CaCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{BaSO}_4$ ,  $\text{KCl}$ ,  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{CsNO}_3$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{LiCl}$ ,  $\text{MgCO}_3$ ,  $\text{K}_2\text{CO}_3$ ?
20. a. Explain why sodium compounds can be and are used more commonly in industry than the corresponding potassium compounds.  
b. What is one major use of potassium compounds in contrast with sodium ones?
21. a. Decide which of the following compounds would tend to hydrolyze most, and write an ionic equilibrium equation for the reaction:  $\text{BeCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ , or  $\text{BaCl}_2$ .  
b. Would the pH of the solution involving the equilibrium above be greater or less than 7?
22. Design and diagram an air-revitalizer kit for a space craft using potassium superoxide,  $\text{KO}_2$ , as the principal chemical.
23. Even though sodium is more active than carbon, the latter can reduce sodium in sodium carbonate at a very high temperature. Write an equation and suggest an explanation for the occurrence of the reaction.
24. Write a chemical equation for the formation of a well-known hydrate formed in the deliquescence of calcium chloride.
25. Magnesium hydroxide is a common medicine, but calcium hydroxide is far too basic to be so used. Explain this difference in properties on the basis of structural arguments.
26. In the Solvay process, calculate the weight of sodium chloride, the weight of limestone, and the weight of ammonia used per ton of sodium carbonate produced, assuming 100 per cent efficiency.
27. To analyze a batch of commercial potassium sulfate, three samples were taken, dissolved in water, and added to separate solutions of barium chloride. The barium sulfate precipitates were filtered, dried, and weighed. The weights of the samples were 0.546, 0.623, and 0.578 g; and the weights of the corresponding precipitates were 0.675, 0.777, and 0.720 g. Calculate the percentage of potassium sulfate in the commercial material.
28.  $\text{NH}_3$  costs more than  $\text{Na}_2\text{CO}_3$  per ton. If you wished to neutralize a ton of  $\text{HCl}$ , which would be cheaper? By how much? Which reaction would produce the most valuable substance? Explain.
29. Write equations and give conditions for the electrolysis of lithium hydride and of strontium hydride.
30. Write equations for the reactions with water of the typical oxides of the first seven elements in period 4 of the periodic table. Indicate whether the product in each case is acidic or basic in water solution.

31. The addition of concentrated hydrochloric acid to aqueous copper sulfate causes the color to change from blue to green. What is the chemical reaction associated with this color change?
32. Direct comparison of electronegativities and oxidation potentials are risky, because the latter involve hydrated ions. But can you see any general relations between these two properties for the several families of metals? (Compare general ranges of oxidation potentials with Fig. 19-1.)
33. Compare the corrosion resistance of aluminum with that of silver.
34. "The oxidation potential of ruthenium is  $-0.45$  volts." What does this suggest with respect to its activity?
35. Show with equations two ways by which each of the following can be prepared:



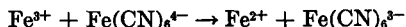
36. Is there a most common oxidation state of the transition metals? Is the periodic table of much value in predicting the oxidation states of these elements? Explain your answer.
37. Using electrochemical equations, explain why the iron in a "tin can" will corrode more rapidly when the surface is broken than the iron in a galvanized can.
38. The magnetic properties of the complex ion  $\text{Ni}(\text{NH}_3)_4^{2+}$  show that it has two unpaired electrons; it is described as an  $sp^3$  complex. Work out an orbital diagram for this complex of the type shown in Table 19-9.
39. Work out orbital diagrams of the type shown in Table 19-9 for the following complexes. The number of unpaired electrons and the type of hybrid orbitals for each are given:

complex	unpaired $e^-$	type of hybrid orbitals
$\text{Cr}(\text{CN})_6^{3-}$	three	$d^2sp^3$
$\text{CoF}_6^{3-}$	four	$sp^3d^2$
$\text{Ru}(\text{CN})_6^{4-}$	none	$d^2sp^3$

40. G. D. Watt, J. J. Christensen, and R. M. Izatt reported the following data in *Inorganic Chemistry*, 4: 220 (1965):

	$\Delta H_r^\circ$ , kcal	$\Delta G_r^\circ$ , kcal
$\text{Fe}^{3+} + 6\text{CN}^- \rightarrow \text{Fe}(\text{CN})_6^{3-}$	-70.14	-59.5
$\text{Fe}^{2+} + 6\text{CN}^- \rightarrow \text{Fe}(\text{CN})_6^{4-}$	-85.77	-48.2

- a. From these data calculate  $\Delta H_r^\circ$ ,  $\Delta G_r^\circ$ , and  $\Delta S_r^\circ$  for the following reaction:



- b. Does the reaction written in (a) tend to take place spontaneously as written? To what is this tendency related, the  $\Delta H$  of the reaction, or the  $\Delta S$ , or both?

**METALS: CHEMICAL PROPERTIES  
AND COMPOUNDS**

41. a. Write the hypothetical stepwise reactions of ethylenediamine with each of the complexes in Table 19-9.  
b. Should any of the compounds formed in the stepwise reactions have isomeric forms?
42. Write balanced equations for the reactions of sodium hydroxide, ammonium hydroxide, and calcium hydroxide with vanadic acid, chromic acid, and perhenic acid, respectively. Name the products.
43. a. How can the formation of a hydrate be regarded as an acid-base reaction? Give an example.  
b. Write the balanced equation for the complete conversion of the hydrate  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  to the ammoniate. Can this be regarded as an acid-base reaction?
44. Does the trend in ionization energy for iron, cobalt, and nickel follow the general trend in the periodic table? Does the trend in oxidation potentials for these three parallel or contrast with the trend in ionization energy?
45. It is reported that freezing-point depression measurements show that  $\text{Co}(\text{NH}_3)_4\text{Cl}_3$  exists in solution in the form of  $[\text{CoCl}_2(\text{NH}_3)_4]^+$  and  $\text{Cl}^-$  ions. Explain in terms of a hypothetical numerical example the sort of data that might have been obtained.
46. a. A standard solution of potassium permanganate can be used to analyze an unknown for the amount of  $\text{Fe}^{2+}$  ion present. The manganese is reduced to the  $\text{Mn}^{2+}$  ion and the iron is oxidized to  $\text{Fe}^{3+}$ . A 0.394-g sample of an iron compound reacted (decolorized) with 26.3 ml of a 0.100 N solution of  $\text{KMnO}_4$ . Calculate the percentage of  $\text{Fe}^{2+}$  in the compound.  
b. What weight of  $\text{KMnO}_4$  would be required to prepare 250 ml of the permanganate solution?
47. Consider a hypothetical covalent compound  $\text{AB}_4$ . What sort of experimental evidence would you seek to determine whether the bonds were of the  $sp^3$  type or the  $dsp^2$  type? (Specific examples are given in Table 17-2.)

**SUPPLEMENTARY READING**

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- Burns, R. M.: "Chemical Reactions in the Corrosion of Metals," *J. Chem. Educ.*, **30**: 318 (1953).
- Manch, W., and W. C. Fernelius: "The Structure and Spectra of Nickel (II) and Copper(II) Complexes," *J. Chem. Educ.*, **38**: 192 (1961).
- Markowitz, M. M.: "Alkali Metal-Water Reactions," *J. Chem. Educ.*, **40**: 633 (1963).
- Petrocelli, A. W., and D. L. Kraus: "The Inorganic Superoxides," *J. Chem. Educ.*, **40**: 146 (1963).
- Sanderson, R. T.: "Principles of Chemical Reaction," *J. Chem. Educ.*, **41**: 13 (1964).
- Vavoulis, A.: "A Spot Test Scheme for the Identification of Metal Ions," *J. Chem. Educ.*, **39**: 395 (1962).

## METALS: NATURAL

## SOURCES, PRODUCTION,

## AND USES



Man's mastery of his environment began when he learned how to produce metals. Whether used in relatively pure form or mixed with one another, the elemental metals are the materials which form the tools and machines of modern civilization. Although most metals are rare, a few are among the most common and useful substances known: elements such as nickel, chromium, tungsten, copper, zinc, silver, tin, and lead. Knowledge and use of these metals made possible the Bronze Age, the Iron Age, and the Industrial Revolution, and they continue to play basic roles, joined by some rarer metals, as the Atomic Age joins the Space Age.

### NATURAL SOURCES OF METALS

*Alkali and Alkaline Earth Elements.* The elements in groups IA and IIA never occur in nature as free elements. Four of them are extremely common: calcium, sodium, potassium, and magnesium ranking respectively as the fifth, sixth, seventh, and eighth most abundant elements in the world. Data on their relative abundances are given in Table 20-1 and Fig. 29-3.

*Abundance of group IA and IIA metals in earth's crust*

TABLE 20-1

element	per cent	element	per cent	element	per cent
Ca	3.4	Ba	$1 \times 10^{-2}$	Be	$4 \times 10^{-4}$
Na	2.6	Sr	$1 \times 10^{-2}$	Cs	$1 \times 10^{-4}$
K	2.4	Rb	$4 \times 10^{-3}$	Ra	$8 \times 10^{-12}$
Mg	1.9	Li	$2 \times 10^{-3}$	Fr	trace

**METALS: NATURAL SOURCES,  
PRODUCTION, AND USES**

The compounds of the alkali elements are so soluble that they tend to be leached out of the soil by rain water and thence carried by streams and rivers to the sea. (The solubilities of some common metal compounds are given in Table 4 in the Appendix.) Sea water contains about 3 per cent by weight of alkali compounds, calculated as the chlorides. Large quantities of alkali salts are found around the world in salt lakes and salt flats, and in underground beds of sedimentary rock left by the evaporation of seas in times long past. There are huge underground domes of almost pure sodium chloride near the Gulf Coast shores of Louisiana and Texas.

The alkaline earth compounds are not quite so soluble as the alkali compounds; indeed, some of the common ones—the carbonates and certain of the sulfates—are insoluble enough to resist the weathering action of rain water strongly. The magnesium ion, however, is one of the very common ions in sea water, and a continuing supply of calcium ion is available in the sea for building the carbonate shells of crustaceous sea animals.

Members of both families of elements are found in igneous rocks as components of practically insoluble minerals, for example, the silicates. The slow weathering of these rocks provides a source of material for the building up of soils and sediments.

*Transition Elements and Their Neighbors.* Of the almost 70 transition metals and their neighbors, the average distribution in the earth's crust of 18 of the most abundant is indicated in Table 20-2.

**TABLE 20-2**     *Abundance of 18 transition metals in earth's crust*

element	per cent	element	per cent	element	per cent
Al	7.5	Zn	$1.3 \times 10^{-2}$	Nd	$2.4 \times 10^{-3}$
Fe	4.7	Ni	$1.1 \times 10^{-2}$	Nb	$2.4 \times 10^{-3}$
Ti	0.6	V	$1 \times 10^{-2}$	Pb	$1.6 \times 10^{-3}$
Mn	0.1	Co	$1 \times 10^{-2}$	La	$6 \times 10^{-4}$
Cr	$2 \times 10^{-2}$	Cu	$1 \times 10^{-2}$	Sn	$4 \times 10^{-4}$
Zr	$2 \times 10^{-2}$	Y	$6 \times 10^{-3}$	W	$1 \times 10^{-4}$

(See also Fig. 29-3.) The relative scarcity of some of the familiar metals is noteworthy; copper, lead, and tin are not so plentiful as zirconium and titanium, two metals unfamiliar to most people.

Many of the relatively rare, precious metals (silver, gold, and the members of the platinum family) are so highly prized because of their strength, beauty, or resistance to chemical attack that they are searched for all over the world. An important characteristic of elements that are rare, yet well known, is that they are relatively easily separated from the minerals in which they occur naturally. By contrast, aluminum, the earth's third most abundant element, was discovered centuries later than gold because of the difficulty of de-

composing its natural compounds. Methods of producing titanium, the tenth most common element, are only now being perfected to the point where it can be produced cheaply. Both titanium and aluminum form such strong bonds with oxygen (in oxides, silicates, and similar compounds) that special chemical methods must be resorted to in separating these elements from their natural compounds.

The most abundant types of ores (for example, oxides and sulfides) are listed in the section on metallurgy, which follows. As we would expect, the very inactive metals are sometimes found in nature in their elemental or free state.

Elements (or their compounds) with similar chemical properties tend to exist together. Zirconium and hafnium are a famous pair because of their likeness to each other. Zirconium was known for years before it was discovered that practically all zirconium minerals contain hafnium also. The "pure" zirconium that chemists had been working with proved to be contaminated with hafnium. Separation of the two is very difficult, because they react in the same ways. Similarly, two or more members of the lanthanide series, so much alike physically and chemically, are usually found together in nature. One of the main sources of the lanthanides for years was *misch metal*, a crude mixture of lanthanum, cerium, and other similar metals recovered during the production of thorium.

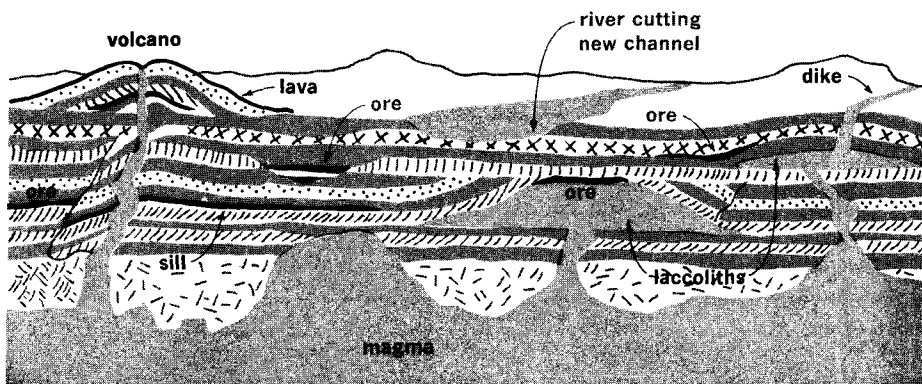
**General Notes on Sources.** Except for magnesium from sea water and some manganese from the floor of the oceans, all metals are produced commercially from the earth's crust, a region discussed in detail in Chap. 29. The natural materials that are found in the earth's crust are called **minerals**. Minerals that can be used as a source for the commercial production of materials are called **ores**.

The most common ores of the metals are *oxides*, *sulfides*, *halides*, *silicates*, *carbonates*, and *sulfates*. The silicates, although the most abundant minerals, are of relatively little value as ores of metals, because they are so difficult to decompose chemically and because there are still available deposits of simpler ores that are easier and cheaper to process.

Ores comprise only a fraction of 1 per cent of the earth's crust. About 95 per cent of the minerals are in the form of *igneous rock*, so-called "original" rock formed by the solidification of molten material and relatively unaffected by erosion or weathering. Igneous rocks formed on the cooling of portions of the *magma* on which the crust of the earth rests. As shown in Fig. 20-1, the magma was forced up here and there through and between layers of the overlying crust. Most of the minerals that form as the magma solidifies are worthless silicates, but the portions of an intrusion that crystallize first or last may contain valuable ores, such as oxides, sulfides, elements, or gem stones. Five per cent of the earth's crust is *sedimentary rock*. Most sedimentary rock is in the form of commercially worthless shales, sand-



## METALS: NATURAL SOURCES, PRODUCTION, AND USES



**FIG. 20-1** Fluid igneous intrusions, forced up from the magma, penetrate beds of sedimentary rock in various ways. Sedimentary beds are folded and fractured by massive shifts in the crust. Valuable ores are relatively rare.

stone, and limestone, but rare valuable minerals are also found in sediments that have been concentrated and deposited by natural geochemical processes.

The relatively rare deposits of valuable oxides, hydroxides, sulfides, and other ores are found all over the world. Rich mineral deposits are the chief wealth of many nations and the basis of much world trade. A distinguishing feature of the high standard of living in the United States is our use of minerals. We consume a fourth of the world's annual production of metals. Much of this is imported—practically all our tin, 90 per cent of our chromium, manganese, and antimony, over three-fourths of our aluminum and nickel, and about half of our zinc and lead.

## PRODUCTION OF METALS

### METALLURGY

The subject of **metallurgy** is concerned with the various processes for obtaining elemental metals from natural ores. These processes are part craft and part science; many of the most useful techniques have been developed over the centuries by trial and error, many more have been discovered more recently by applying advanced theories and the latest knowledge.

The general problem of metallurgy is to decompose a compound in which a metal exists in a positive oxidation state, often as positive ions, and to transform the positive ions of the metal into atoms, that is, into the element. A general simplified equation,  $x$  being 1, 2, 3, etc., is

The typical reaction is a reduction reaction. The metal in its positive oxidation state is not necessarily a simple ion; indeed, it is often found in an anion with oxygen, for example,  $\text{MO}_4^{2-}$ , or in a silicate.

In rare cases, the desired metal is found in the elemental state and hence needs only to be separated from impurities.

The metallurgy of most metals has three main parts: (1) concentration of the ore, (2) chemical reduction to the element, and (3) refining and purifying. In some cases these activities overlap; for example, chemical reduction can be part of the concentration process or of the refining operation.

**Concentration of Ore.** The ore that is mined usually contains some worthless rock called *gangue*. If the gangue is objectionable at a later stage, the first step in ore concentration is to remove it. The ore is usually crushed and ground till the particles of the mineral are broken apart from the gangue. If possible, these particles are separated by physical means, such as washing, flotation, or magnetic attraction.

**Washing** with a turbulent stream of water often washes the lighter gangue away from the desired mineral.

**Flotation** involves agitating the ore in a vessel with a detergent or foaming agent. The more valuable denser mineral may stick to the bubbles of foam and float off with it, leaving the gangue behind, or the gangue may be attracted to the foamy layer and floated off with it. (See Fig. 20-2.)

With an *electromagnet* some minerals can be drawn out of their crushed ores. An example is magnetite,  $\text{Fe}_3\text{O}_4$ . Also, certain minerals

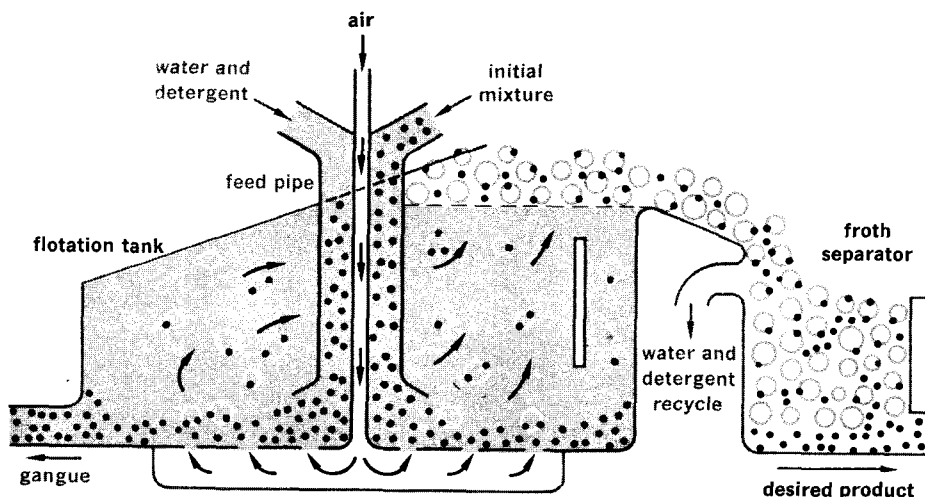


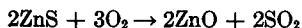
Diagram of a flotation tank showing the separation of a desired material (colored). A rotating paddle at the bottom of the cell distributes the feed and also sweeps the bubbles around the central pipe.

FIG. 20-2

can be charged electrically and then attracted to a charged plate, leaving the gangue behind. (This technique is similar to that employed in the Cottrell precipitator described in Chap. 11.)

If the ore cannot be sufficiently concentrated by physical means, chemical processes are used, such as those described in the following paragraphs.

In many cases the ore is *roasted* to drive off volatile impurities and to burn off organic matter. Roasting in air usually converts sulfides and carbonates to oxides. For example:



Ores generally contain considerable gangue, even after the most careful physical separation. Often, to remove the last of the gangue, a *flux* is added. When the mixture is heated in a furnace, the flux combines with the gangue and makes a molten material called *slag*. At high temperatures, the slag is a liquid that is insoluble in the molten metal, hence the two can be separated. If the gangue is an acidic oxide, such as silica,  $\text{SiO}_2$ , a cheap basic oxide like lime,  $\text{CaO}$ , will be used for the flux. These two react in a furnace to form the low-melting compound calcium silicate, the slag:

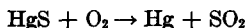


If the gangue is basic, for example, calcium or magnesium carbonate, the flux will be a cheap acidic oxide.

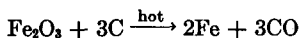
Acids or bases may be used to *dissolve* part of the ore. Sometimes a compound of the desired metal is precipitated from the solution; sometimes impurities are precipitated.

**Reduction to the Element.** There are several chemical methods that can be used to reduce a given metal from its oxidation state in the ore to the elemental state. If reduction is difficult for a particular metal, powerful reducing processes will be necessary.

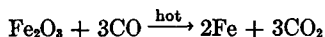
**REDUCTION BY HEAT IN AIR.** The precious metals in groups VIIIB and IB are produced easily. Platinum, gold, and sometimes silver are found in their elemental form and have only to be heated to melt them out of the gangue. Because many of the oxides of the less active metals are decomposed by extreme heat, roasting in air is all that is needed for reduction. For example, roasting the sulfide ore of mercury forms the metal rather than the metallic oxide:



**REDUCTION WITH CARBON.** Oxides of many moderately active metals can be reduced by carbon. The reaction for iron oxide is



or

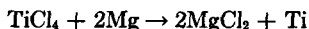


This reduction method is suitable for metals of the iron family and for some others, such as lead, tin, and zinc. Note that the carbon may

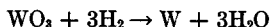
be oxidized to carbon monoxide, CO, or carbon dioxide, CO<sub>2</sub>. In many cases, as for iron in the reactions above, the carbon monoxide formed acts as a reducing agent.

Carbon tends to form carbides with certain metals, such as chromium and manganese, hence it cannot be employed for the reduction of all oxide ores. But it is used when possible, because it is both cheap and convenient.

**REDUCTION WITH AN ACTIVE METAL.** If compounds are not satisfactorily reduced with carbon, a more active metal can be used as the reducing agent. Aluminum, magnesium, sodium, and calcium are active enough to be good reducing agents. Uranium(IV) fluoride is reduced with calcium. Titanium chloride is reduced by magnesium or sodium:



**REDUCTION BY HYDROGEN.** Reduction by hydrogen is more expensive than reduction by carbon and is only used when carbon is not suitable. Tungsten oxide is reduced in this way:



**REDUCTION BY ELECTROLYSIS.** Very active metals, such as the alkali metals and the alkaline earth elements, are most efficiently produced by the electrolysis of anhydrous fused salts.

In addition to these metals, the group IIIB elements and the lanthanide series are usually prepared by electrolysis of fused salts. The chlorides are commonly used for this purpose.

**Refining and Purifying.** The metal produced commercially by any of the methods above usually contains considerable amounts of impurities.

Metals with low boiling points—for example, mercury, bismuth, and tin—can be separated from most impurities simply by melting the metal and pouring it off or by distilling it. Like salts, metals can also be refined by fractional crystallization.

Probably the most widely used refining process is the electrolytic process. Copper is typical of the metals refined by this method, as we shall see in detail shortly.

## **METALLURGY OF COMMON METALS**

We shall now discuss the production of several of the most important metals in order to illustrate metallurgical principles.

One of the metals, copper, is relatively inactive. It is reduced by heating its most common ore, the sulfide, to a high temperature in air.

The second metal, iron, is moderately active, but its compounds can be reduced cheaply by carbon or carbon monoxide. For commercial production its ore, iron oxide, is reduced at a high temperature by carbon monoxide.

The third metal, aluminum, is very active chemically. Its refined ore, aluminum oxide, cannot be reduced satisfactorily and economically by more active substances. Only electrolysis is feasible for its commercial reduction.

Finally, we shall say a word about the production of the very active metals, such as magnesium and sodium. It is interesting to note that historically these several metals were produced in a logical order—the easily reduced copper first, the difficult active metals last.

**Copper.** Down through history to the present time, copper and its alloys have been regarded as standards of permanence. Coins, statues, roofs, gutters, cannon, gun cartridges, cooking utensils, and many other objects exposed to a variety of conditions have been made of copper or its alloys. The Statue of Liberty, containing 25 tons of metal, is the largest copper statue in the world.

The mineral deposits of copper can be grouped in three classes: the ores containing veins and nuggets of native (elemental) copper, those containing some form of copper-sulfur compound, and those containing some form of copper-oxygen compound.

The sulfide ores account for about 70 per cent of the copper output of the United States. In the early days of the copper industry in this country, rich finds were made near the Great Lakes and in the Western states. Ores containing a high percentage of native copper or copper compounds were mined. Today relatively little native copper is mined, most of the metal being produced from ores that are about 1 per cent available copper. Whole mountains may be quarried to get at ore that averages less than 0.5 per cent copper.

The treatment of an ore depends on the amount and kind of impurities and the desired purity of the product, among several other factors. We shall consider only the copper sulfide ore. Usually three operations are necessary to obtain pure copper: concentrating, smelting, and refining.

**CONCENTRATING.** The raw ore is passed through a series of crushers and grinders that reduce it to a coarse powder. The individual particles of gangue (chiefly silicates) and copper sulfide are separated by flotation (Fig. 20-2). An interesting fact here is that the sulfide particles that float to the surface in the foam are denser than the particles of silicate gangue that settle to the bottom.

The foam is swept from the top of the flotation vessel into a settling tank, where the impure copper sulfide is separated from most of the water by filtration. The concentrated solid also contains iron oxide, iron sulfide, some gangue, and traces of many other metals including gold and silver.

**SMELTING.** The sulfide concentrate is heated in a furnace or oven, possibly 100 ft long and 30 ft wide, by hot gases produced by burning coal dust. The two compounds,  $\text{Cu}_2\text{S}$  and  $\text{FeS}$ , form a mixture called *matte*. The extreme heat of the furnace melts the matte and the

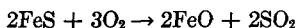
gangue. Usually the gangue is composed mainly of acidic oxides, such as  $\text{SiO}_2$ , but it may be basic; that is, it may contain  $\text{CaO}$  from  $\text{CaCO}_3$ . If the gangue is acidic, calcium carbonate is added; if it is basic, silica is added. The molten product in either case is a calcium silicate slag,  $\text{CaSiO}_3$ , that melts easily and floats at the top of the liquid matte.

After the molten matte settles to the bottom of the furnace, it is drawn off separately into a converter. Some of the iron that is present as iron oxide combines with the gangue to form a silicate:

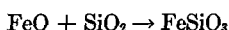


that floats off with the rest of the slag. Any iron sulfide, however, tends to remain with the copper sulfide matte.

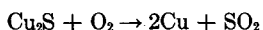
The separation of the iron and copper depends on the fact that  $\text{FeS}$  is attacked by oxygen more readily than  $\text{Cu}_2\text{S}$  is. A measured amount of  $\text{SiO}_2$  is added to the liquid in the converter. Air under high pressure is blown through the molten mixture, resulting in the oxidation of the iron sulfide to iron oxide and gaseous sulfur dioxide:<sup>1</sup>



The oxide combines with the added sand, forming a slag:



After the slag is drained off, more air is blown through the molten copper sulfide:



The elemental copper is poured into molds, where it cools. It is now known as "blister copper" because of its appearance, which is due to the bubbles of  $\text{SO}_2$  gas formed during solidification.

Blister copper may be as high as 99 per cent pure. It can be used in this form for the production of many items, such as alloys and building materials. However, almost three-quarters of it is refined.

**REFINING.** To be acceptable to the electrical industry, copper must be at least 99.95 per cent pure. Over 1.5 million tons of this high-quality metal are produced electrolytically in the United States each year.

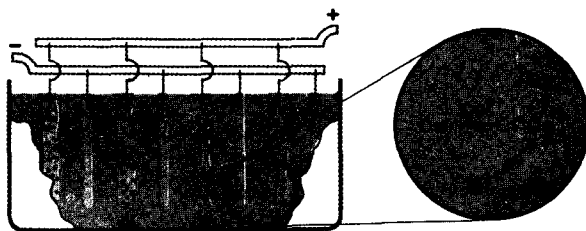
The blister copper (containing about 1 per cent total impurities) is made the anode in an electrolytic bath, and a thin sheet of pure copper is made the cathode. The electrolyte is a solution of copper sulfate and sulfuric acid. As electrolysis proceeds, copper dissolves from the anode, forming copper ions. These diffuse through the electrolytic bath and are plated out on the sheet of pure copper, which serves as the cathode (see Fig. 20-3). Thus, the slab of blister copper

<sup>1</sup> Today, modern smelting companies not only remove the  $\text{SO}_2$  from the waste gases but make sulfuric acid,  $\text{H}_2\text{SO}_4$ , from it. What was once a useless, destructive by-product is now their main source of profit; at one time these companies produced from it 10 per cent of the sulfuric acid made in this country. Other chemical concerns have not been so fortunate in regard to their by-products and waste products; some continue to pollute our streams and atmosphere with noxious materials.

is dissolved slowly, and the thin sheet of copper that serves as the cathode builds up to a large slab of relatively pure copper.

Metal impurities in the blister copper anode may be classified in four groups: (1) silver, gold, platinum, palladium; (2) sulfur, selenium, tellurium; (3) arsenic, antimony, bismuth; and (4) lead, tin, nickel, cobalt, iron, zinc. As the anode dissolves during electrolysis, the impurities either precipitate to the bottom of the bath or go into the electrolyte as ions.

At the operating voltage of the bath, the noble metals like gold and platinum do not tend to form positive ions.<sup>1</sup> They collect at the bottom in the "anode mud," an unglamorous name for a most valuable by-product. From 2 to 200 oz of silver and from a trace to 6 oz of gold are recovered per ton of copper in the anode. Elements of the sulfur family are also found in the anode mud in the form of insoluble precipitates, such as  $\text{Cu}_2\text{S}$ ,  $\text{Cu}_2\text{Se}$ ,  $\text{Ag}_2\text{S}$ , and  $\text{Ag}_2\text{Te}$ .



The electrolytic refining of copper. Noble metal impurities are indicated as black dots. As the anodes are dissolved away, the cathodes grow in size.

FIG. 20-3

Arsenic, antimony, and bismuth are the chief troublemakers among the impurities. Arsenic especially may dissolve at the anode, pass through the electrolyte as an ion, and deposit with the copper. The presence of even a minute amount of arsenic is serious, because arsenic lowers the electrical conductivity of copper. Adjusting the voltage of the bath and keeping the concentration of  $\text{Cu}^{2+}$  ion high holds the deposition of arsenic in the cathode to a minimum.

The metals above copper in the electromotive series, such as iron, nickel, and zinc, dissolve from the anode as cations,  $\text{M}^{2+}$ . The voltage of the bath is kept low enough so that these elements remain in solution. As they accumulate, the impure electrolyte is drawn off for salvage and replaced with fresh sulfuric acid and copper sulfate. The reactions may be summarized thus, M being Zn, Fe, Co, Ni, Pb, Sn:

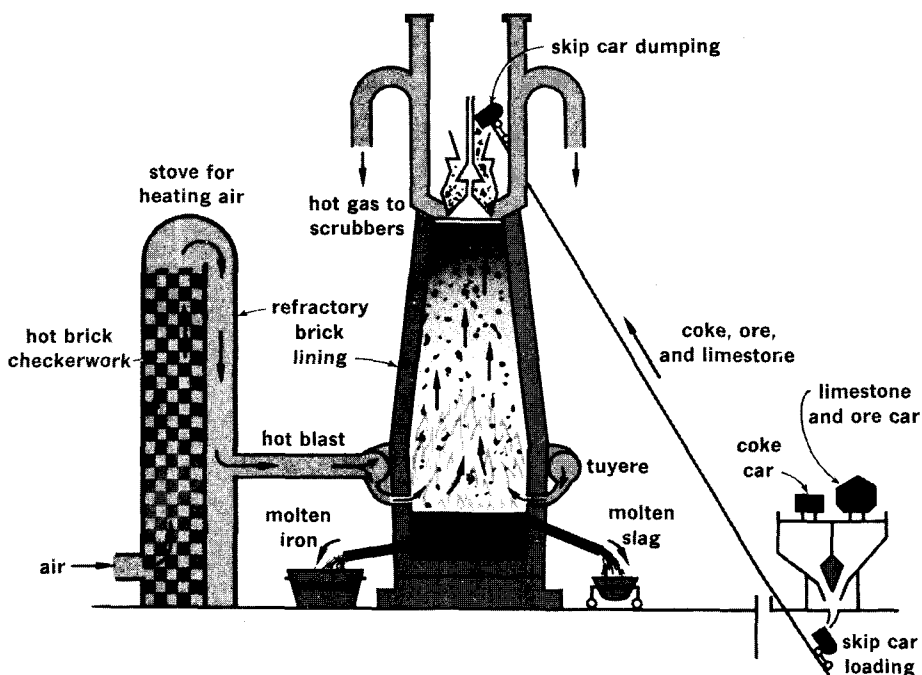
At the anode:



At the cathode:



<sup>1</sup> Some silver may dissolve as silver ions, but the bath contains  $\text{Cl}^-$  ions that join the  $\text{Ag}^+$  ions to precipitate as insoluble silver chloride.



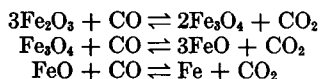
Schematic diagram of a blast furnace. (Courtesy of Bethlehem Steel Company.)

FIG. 20-4

**Iron.** One of man's most important technical advances was his discovery of methods of separating iron from its ores. The use of iron and its most important alloy, steel, transformed man's way of life directly and completely.

The changing of iron oxide ores into iron was first an art, later an intensively studied science. So much is known and so much is being done in this field that the study of the metallurgy of iron and its alloys is a lifework.

Iron is a good example of the moderately active metals that are reduced by carbon monoxide. The common oxide of iron,  $\text{Fe}_2\text{O}_3$ , is reduced to the element in a series of steps:

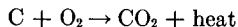


**BLAST FURNACE.** The primary reduction of the iron oxide ore is carried out in a mammoth chimney called a *blast furnace*. In this fiery reaction chamber molten iron is formed, and silica,  $\text{SiO}_2$ , the chief impurity, is largely removed. Lime,  $\text{CaO}$ , added in the form of calcium carbonate, combines with the silica to form slag. As shown in Fig. 20-4, the molten slag and iron settle in separate layers at the bottom of the furnace.



**METALS: NATURAL SOURCES,  
PRODUCTION, AND USES**

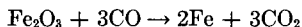
A mixture of crushed iron ore, coke, and limestone is added by means of a hopper at the top of the furnace. A blast of hot air is blown up through this mixture from the bottom of the furnace. The complex series of reactions can be summarized as follows. Near the bottom of the furnace, where the blast of hot air enters, coke burns furiously:



As the carbon dioxide rises in the chimney, it is reduced almost immediately by hot coke:



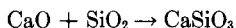
The carbon monoxide reacts with the iron oxide to form metallic iron in the series of steps described in the last section. These reactions, which occur in the middle and upper portions of the furnace, can be summarized by the overall equation



Near the middle of the furnace, the limestone decomposes to form lime and carbon dioxide:



Farther down, the lime and silica react to form a slag:



The operation of the furnace is continuous; the mixture of reactants is fed into the top at regular intervals to begin its journey toward the white-hot lower levels. The temperature near the bottom is high enough to melt the iron and slag, and they collect as immiscible layers at the bottom. The furnace must be "tapped" about every six hours to drain off the molten iron.

For each ton of blast furnace iron, or pig iron,<sup>1</sup> produced, there are required about 2 tons of iron ore, 1 ton of coke, 0.3 ton of limestone, and 4 tons of air. The main by-products are 0.6 ton of slag and 5.7 tons of flue gas.

There are approximately 250 blast furnaces in this country and the average daily production of pig iron per furnace is 800 tons. The largest modern furnaces have a capacity of more than 1,500 tons a day.

The hot flue gas is valuable as a fuel. It is mainly nitrogen and carbon dioxide, but contains about 12 per cent CO and 1 per cent H<sub>2</sub>. Both of the latter, when burned, yield heat energy for a variety of uses, such as the following: to fire the stoves in which the incoming air for the blast is heated; to produce steam for power to move the raw materials to the furnace, blow the air, etc.; to fire the furnaces in which coal is changed to coke, and those in which the pig iron is converted into steel.

<sup>1</sup> The molten blast furnace iron is sometimes run into molds, where it hardens into small ingots called *pigs*. However, much of the molten iron is converted directly into steel, instead of into ingots or pigs. The terms *pig iron* and *blast furnace iron* are synonymous.

Schematic diagram of a Bessemer converter during a blow; the pouring position is also indicated. (Courtesy of Bethlehem Steel Company.)

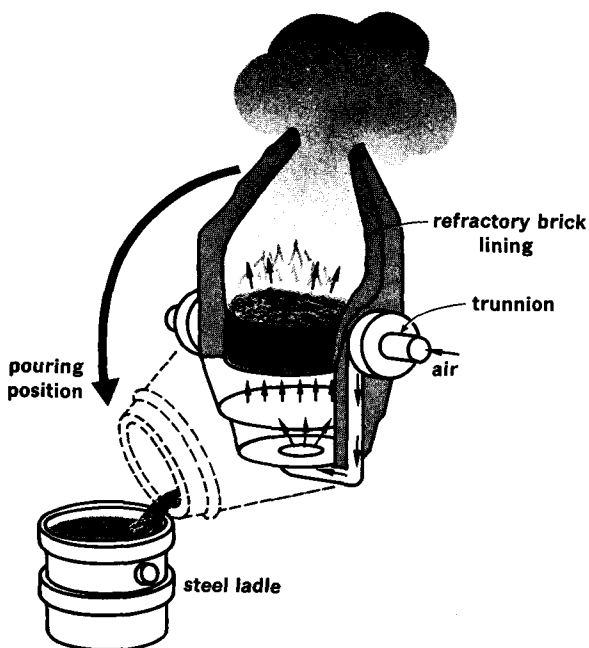


FIG. 20-5

**IRON AND STEEL.** Pig iron is so brittle and so low in tensile strength that it is of little use. Its poor quality is due chiefly to the presence of several impurities: 3 to 5 per cent carbon and smaller percentages of silicon, phosphorus, and sulfur.

Melting pig iron and high-grade scrap iron together produces *cast iron*. It has about 2 per cent miscellaneous impurities, chiefly carbon, but is too brittle to be forged, rolled, or welded. Articles made from it are cast into the desired shape in a mold.

Most iron is made into *steel*, an alloy which contains 0.05 to 2.0 per cent carbon and which can be made tough as well as hard by special heat treatment. To make steel from pig iron, some of the carbon and practically all the phosphorus, sulfur, and silicon must be removed.

One of the first methods of making steel was invented in England in 1856 by Sir Henry Bessemer. In the Bessemer process, about 25 tons of molten pig iron is poured into a huge egg-shaped *converter* (Fig. 20-5) that has a perforated bottom through which compressed air is blown. As the blast of hot air bubbles through the molten iron, the carbon is oxidized to carbon dioxide and escapes. By the appearance of the fiery blast as it issues from the converter, an experienced operator can tell when to cut off the air. For too much air causes oxidation of the iron; furthermore, a small amount of unburned carbon must be left in the steel. After a "blow," which lasts from ten to

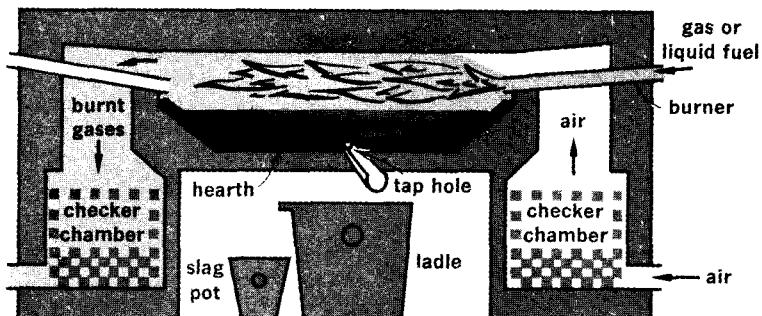


FIG. 20-6

Schematic diagram of an open-hearth furnace for steel production. (Courtesy of Bethlehem Steel Company.)

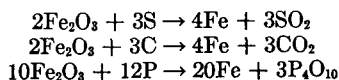
fifteen minutes, small amounts of manganese, carbon, and other alloy materials are added to the molten iron to produce steel.

The spectacular blow of the Bessemer converter was the trademark of the early steel industry in this country. Steel from these furnaces was used in the railroads that spanned the continent and in the factories that industrialized the nation.

However, the Bessemer converter is not well suited for the purification of pig iron that contains phosphorus and sulfur. Moreover, the key reactions take place during the short and violent "blow"; hence a fine and careful adjustment of the percentage of carbon and other alloying elements is not possible.

The *open-hearth* method of making steel largely displaced the Bessemer process; it now accounts for most of the steel produced in this country. The average hearth (Fig. 20-6) is a shallow vessel 40 by 18 ft and 2 ft deep. Over it is a roof of arched fire brick against which hot fuel gases are burned. The materials charged into the hearth are pig iron, rusty scrap iron ( $\text{Fe}_2\text{O}_3$  on the surface) or smaller amounts of iron ore, and other materials for special alloys.

The hearth is lined with either a basic or an acidic lining, depending on the type of pig iron being purified. In this country the ores usually have acid impurities (phosphorus or sulfur), so that basic linings, such as magnesium and calcium oxide, are used. When the charge of 100 or more tons is melted in the hearth, the iron rust (or iron ore) may take part in the following typical reactions:



The  $\text{CO}_2$  gas bubbles out of the melt, and the sulfur and phosphorus oxides combine with the basic oxides of the lining to form a slag.

The process is slow enough (about eight hours) so that classical, rather slow chemical analyses can be made periodically to check the composition of the steel. This greater control of composition is perhaps

the chief advantage of the open-hearth process over the Bessemer.

At one time the open-hearth process accounted for about 90 per cent of United States steel production. New methods, such as the *electric furnace* and *basic oxygen furnace* processes, now account for about 15 per cent of the production. Features of these methods are the use of high-pressure oxygen to burn out excess carbon and the use of modern instruments to make very rapid chemical analyses of the molten steel. By using computers to interpret the complex emission spectra of samples, the composition of the melt can be determined in a few minutes, the proper substances can be added, and the steel poured in about an eighth of the time needed for the open-hearth process. Steel production in the United States is about 100 million tons annually.

**Aluminum.** Aluminum is the most common metallic element in the earth's crust, but it was not till 1886 that the electrolytic process was invented for recovering aluminum from its ores. Because aluminum ions are more difficult to reduce than hydrogen ions, the electrolysis cannot be carried out in a water solution. Several chemists had tried to devise a method of electrolyzing aluminum halides in fused salt baths (analogous to producing other active metals like sodium and magnesium). But the aluminum halides have such low melting and boiling points<sup>1</sup> that they tend to distill out of high-temperature baths. Avidly sought by able chemists for many years, the successful commercial process was discovered practically simultaneously by two investigators, Charles M. Hall in this country and Paul Héroult in France.

The process devised by the twenty-two-year-old Hall is practically identical to that used commercially today. Anhydrous  $\text{Al}_2\text{O}_3$  is dissolved in cryolite, where it is thought to be in the form of the ions  $\text{Al}^{3+}$  and  $\text{O}^{2-}$ . Electrolysis of the solution yields elemental aluminum at the cathode and oxygen at the anode.

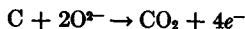
A schematic diagram of electrolytic cells for the production of aluminum is shown in Fig. 20-7. An iron tank lined with carbon is the cathode of the cell, and large blocks of carbon serve as anodes. The cryolite is melted in the tank, and purified anhydrous aluminum oxide (alumina) is added to it.

When current is passed through the cell, molten aluminum forms at the walls and bottom of the tank (the cathode). Essentially all the oxygen liberated at the anode attacks the carbon and forms carbon dioxide:

At the cathode:



At the anode:



<sup>1</sup> They are more covalent than most metal halides, owing to the high charge density of  $\text{Al}^{3+}$ .

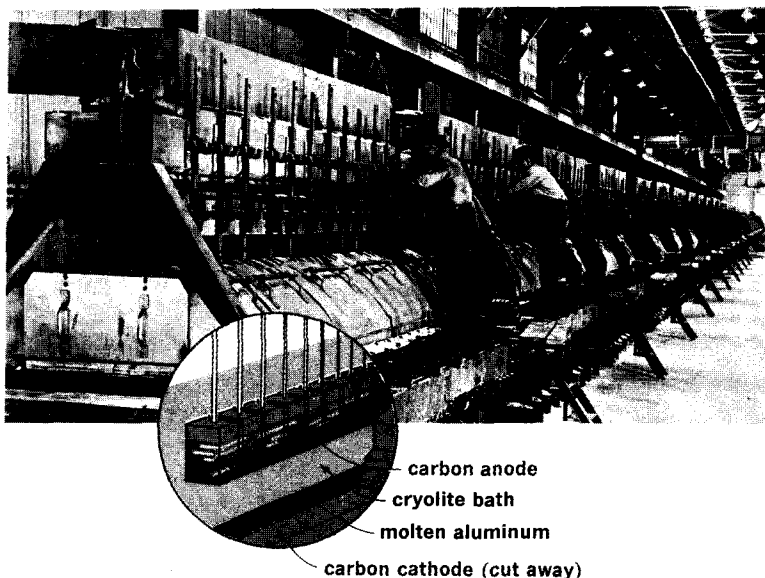


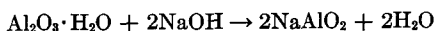
FIG. 20-7

Alumina electrolysis "pots." (Photograph courtesy Aluminum Company of America.)

The passage of the electric current through the cryolite generates enough heat to keep it melted. The temperature, about  $1000^{\circ}\text{C}$ , is above the melting point of aluminum, so that the metal produced collects in the bottom of the cell as a liquid. Periodically, the molten aluminum is siphoned off into molds, cooled, and formed into large ingots.

No commercial process has been developed whereby aluminum can be obtained from the plentiful aluminum silicate minerals. The raw material for the Hall process is *bauxite*, a mineral that consists mainly of hydrated aluminum oxide (for example,  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  and  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ). There are valuable deposits of it in Arkansas, but we import large quantities from South America and Jamaica.

The bauxite is carefully purified to remove the traces of iron and any other metals present.<sup>1</sup> Purification involves dissolving the bauxite in hot sodium hydroxide to form sodium aluminate:



In this reaction the *amphoteric* aluminum oxide reacts as an acidic oxide. The other metal oxides, such as iron, form insoluble hydroxides and are separated by filtration.

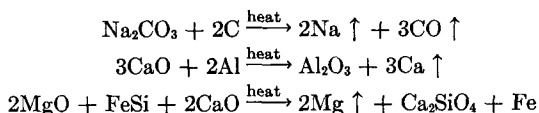
When the sodium aluminate solution is cooled and seeded with small crystals of the desired precipitate, pure hydrated aluminum

<sup>1</sup> A higher voltage is necessary to reduce  $\text{Al}^{3+}$  than is required for the reduction of most other metallic ions. Therefore, most metallic ion impurities left in the bauxite would be reduced along with the aluminum ions and appear as impurities in the metal.

oxide crystallizes. After it is completely dehydrated (by heating it to over 1000°), it is ready for the electrolysis cell.

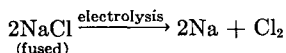
The aluminum produced by the primary electrolysis is better than 99 per cent pure; further electrolytic refining gives metal that is more than 99.9 per cent pure.

**Sodium and Magnesium.** SIMPLE CHEMICAL ACTION. Because of the extremely low electronegativities of the group IA and IIA elements it is difficult to find other substances from which their ions can gain electrons. However, at high temperatures these positive ions will take electrons from some elements that are inherently more electro-negative. One of the reasons for such reactions is that at least one of the products has a relatively low boiling point, so that it vaporizes as it forms and leaves the reaction mixture as a gas. In such a change the entropy is increased; as we saw in Chap. 16, any reaction for which  $\Delta S$  is positive tends to occur if the temperature is high enough (that is, if  $T\Delta S$  becomes large enough). Examples of older methods used to produce active metals are



**ELECTROLYSIS.** By far the most practical and widely used method for the reduction of active metals is the *electrolysis* of fused hydroxides or chlorides. The chloride is generally employed in the United States. Large amounts of elemental sodium, magnesium, and calcium are produced in this way.

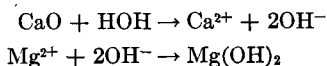
In the case of sodium chloride the reaction is



Chlorine gas is a valuable by-product of this process.

So far as the alkali metals are concerned, there are two reasons why sodium is the only one produced on a very large scale: (1) the raw material (NaCl) required for its production is available in enormous high-purity deposits at many places in the earth's crust, and (2) it serves equally well for most industrial purposes in place of the more expensive alkali metals.

The preparation of magnesium by the electrolysis of molten magnesium chloride must be preceded by the preparation of the chloride, because there are no deposits of relatively pure magnesium chloride as there are of sodium chloride. One method starts with sea water, which contains a practically inexhaustible supply of magnesium ions. The magnesium is first precipitated as magnesium hydroxide by the addition of lime to the sea water:



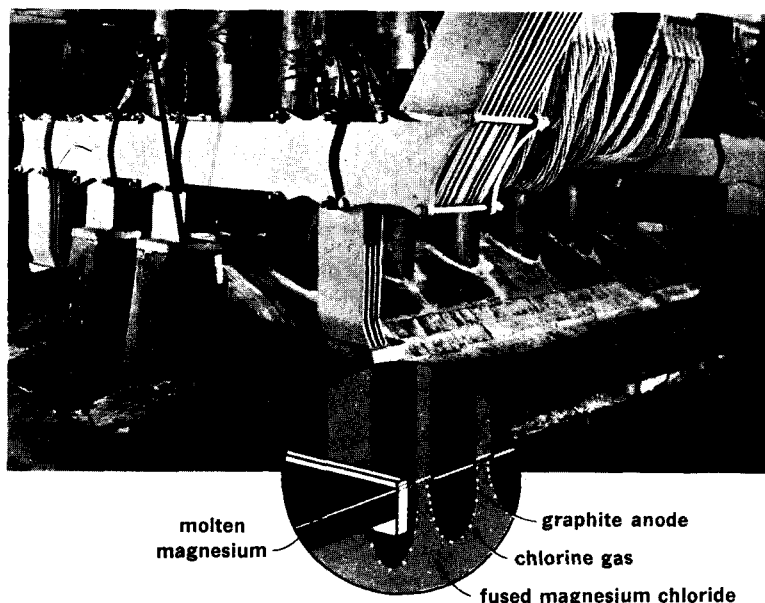
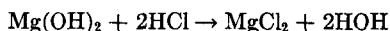


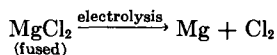
FIG. 20-8

The production of magnesium by electrolysis of molten magnesium chloride. The molten magnesium, formed at the anodes, rises at the sides and is separated from the chlorine by a metal barrier. (Photograph courtesy The Dow Metal Products Company.)

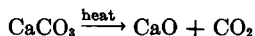
The magnesium hydroxide is removed by filtration and then converted into the chloride by the addition of hydrochloric acid:



After the water is removed by evaporation, electrolysis of the magnesium chloride is carried out in a large steel pot that serves as the cathode; graphite bars immersed in the molten magnesium chloride serve as the anodes (Fig. 20-8). As the molten magnesium forms, it floats to the surface and is removed at suitable intervals:



The chlorine is recovered and converted into hydrochloric acid for use in a previous step of the process. It is interesting to note that the coastal region of Texas, one place where this process is carried out, has no deposits of limestone rock, the usual source of calcium carbonate for the production of lime. However, oyster shells, which are abundant and rich in calcium carbonate, are calcined to supply the lime:



Production of magnesium in the United States is about 50,000 tons annually.

## USES OF METALS

### ALLOYS

Although there are only about 80 metal elements, there are thousands of different combinations of them, each with its own special properties. Metals have the ability to mix with and combine with one another to form a practically unlimited number of alloys. An alloy is the solid that results when two or more metals are melted together to form a homogeneous mixture and then allowed to cool.

The metals in an alloy may form as follows: (1) They may dissolve completely in one another and on cooling form a *solid solution* (homogeneous). (2) They may crystallize separately and be present in the alloy as a *mixture* of tiny crystals (heterogeneous). (3) Their atoms may combine in a definite ratio, forming an *intermetallic compound* (homogeneous).

The transition elements form a great variety of alloys.

**Properties of Alloys.** Alloys have properties of their own that often differ markedly from those of the elements of which they are made. For example, the melting points of some alloys—for example, solder—are lower than that of any of their constituents. Other alloys have higher melting points than do any of their constituents.

Alloys are usually harder than the parent metals. Pure iron is quite soft and ductile in comparison with the steel alloys, which are composed mainly of iron. Gold is too soft even for jewelry; it must be hardened by alloying with copper or some other metal. Alloys are generally poorer conductors of heat and electricity than pure metals.

One of the chief differences between pure metals and alloys is corrosion resistance. Alloys are usually more resistant to corrosion; hence they are more useful for materials that are exposed to the action of corrosive agents. Aluminum alloys are notable exceptions to this; they are sometimes covered with pure aluminum to improve their corrosion resistance.

In spite of the important differences between elemental metals and alloys, there are some important similarities. Alloys usually have to some degree the metallic properties of heat and electrical conductivity, ductility, and malleability, and they show a metallic luster.

As methods for producing some of the rarer metals are perfected, research will undoubtedly lead to the formulation of more valuable alloys than we have today. A great deal of scientific research is at present being devoted to the study of alloys for use in high-temperature jet and rocket engines and in nuclear energy power plants. Table 20-3 lists some alloy steels, together with their composition and uses. Some of the nonferrous alloys are listed in Table 20-4.



**TABLE 20-3**     *Alloy steels (carbon content from 0.08 to 0.8 per cent or more)*

alloy	amount of alloy metals	special characteristics	important uses
nickel steel	3.5% Ni	hard, tough	rock drills, crankshafts, armor plate
chrome steel	1% Cr	strong, tough	springs, wood-cutting tools
stellite	30% Co, 14% W, 4% Cr	holds hardness at high temperatures	high-speed cutting tools, surgical instruments
nickel-chromium steel	1-3.5% Ni, 0.2-1.5% Cr	strong, surface easily hardened	piston rings and pins, gears, armor plate, ball bearings
stainless steel	18% Cr, 8% Ni	corrosion-resistant, hard	surgical instruments, kitchenware, stainless cutlery
high-speed steel	18% W, 4% Cr, 1% V	holds hardness at high temperatures	high-speed cutting tools
manganese steel	12-14% Mn	hard, resistant to wear, holds temper	grinding machines, safes, jaws of rock crushers and power shovels
chrome-vanadium steel	2-10% Cr, 0.1-0.2% V	tough and elastic, fatigue-resisting	automobile axles, frames, connecting rods
duriron	14.5% Si, 0.35% Mn	brittle, corrosion-resistant	plumbing for chemical wastes

## IRON AND STEEL

Iron, one of the seven metals known to the ancients, is our most widely used metal. Yet few people have seen pure iron. A silvery-white metal, it corrodes rapidly, is moderately soft, has low tensile strength, and is ill-suited as such for many of the uses commonly ascribed to it. Most so-called iron objects are carbon steels and alloys.

**Carbon Steel.** The great bulk of steel used today is *carbon steel*. This term covers a multitude of steels, ranging from the softest, mildest steels, which are nearly pure iron, to the high-carbon steels used in making tools. (However, alloy steels are gradually replacing carbon steels as materials for tools.) Enormous quantities of carbon steel are required for railroads, bridges, ships, the framework of factories and large buildings, and automobiles and trucks. It is the steel from which hundreds of everyday articles are fabricated. Structural and general-purpose carbon steels contain about 0.15 to 0.40 per cent carbon. Alloy metals—nickel, chromium, vanadium, tungsten, etc.—are not present in appreciable amounts. Such steels may contain manganese, silicon, and copper in amounts up to 1.65, 0.60, and 0.60 per cent, respectively, but they usually contain a considerably smaller amount of these elements. Structural carbon steel has a tensile strength of about 40 tons/in.<sup>2</sup>, is relatively soft, and has good workability.

*Nonferrous alloys*

TABLE 20-4

name	percentage composition (approximate)	use
babbitt	Sn 85, Sb 10, Cu 5	bearings
brass, red	Cu 85, Zn 15	hardware, radiator cores
brass, yellow	Cu 67, Zn 33	musical instruments, cartridges
bronze, ordinary	Cu 90, Sn 10	valves, rods
bronze, aluminum	Cu 90, Al 10	gilt paint
bronze, phosphor	Cu 95, Sn 4.8, P 0.2	spring metal
gold, white	Au 75, Cu 3.5, Ni 16.5, Zn 5	jewelry
Linotype metal	Pb 79, Sb 16, Sn 5	printing
nickel silver	Cu 64, Ni 18, Zn 18	silverware, plating, resistance wire
pewter	Sn 85, Cu 7, Bi 6, Sb 2	metal dishes
René 41	Ni 55, Cr 19, Co 11, Mo 10, Ti + Al 5	sheathing of space capsules, jet engines
solder, soft	Sn 60, Pb 40	solder
sterling silver	Ag 92.5, Cu 7.5	silverware
Wood's metal	Bi 50, Cd 12.5, Pb 25, Sn 12.5	low-melting alloy, fuses

**Alloy Steels.** Hard carbon steels are much too brittle for structural use or for the manufacture of machine parts. Alloying steel with nickel, chromium, manganese (in excess of 1.65 per cent), tungsten, vanadium, and other metals produces *alloy steels*. These steels range in tensile strength as high as 110 tons/in.<sup>2</sup>, can be made uniformly hard, are not brittle, and have other desirable properties. A vast number of such steels are on the market today; in general, however, they are more expensive and more difficult to work than carbon steels.

**COBALT AND NICKEL**

Iron, cobalt, and nickel constitute a family in the periodic table and have many properties in common. For example, their melting and boiling points and their densities are very close, and all three elements form colored salts and complex ions.

Unlike iron, nickel is resistant to atmospheric corrosion. It has been used as a plating material to protect iron and other metals against corrosion and to improve their appearance. Chromium is largely used now for this purpose, although an underplate of nickel is frequently applied preparatory to plating with chromium. Most of the nickel and cobalt now produced goes into alloy steels.

Finely divided nickel is an effective catalyst for the reaction of hydrogen with molecules of organic compounds. Oleomargarine and vegetable shortening (for example, Snowdrift and Crisco) are made by such processes.

## **COPPER, SILVER, AND GOLD**

Copper, silver, and gold, members of the IB family, are among the oldest metals known to man. Gold ornaments have been found in burial places that date back to the Stone Age. The use of copper for utensils is believed to have begun during that period. Because these three metals have been used for many centuries in making coins, they are sometimes referred to as the *coinage metals*.

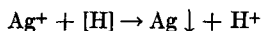
Discovery of methods of alloying copper to make bronze, a harder material, gradually led to the replacement of stone with bronze as a material for tools and weapons and ushered in the period known as the Bronze Age. Bronze is an alloy of copper and tin; brass is an alloy of copper and zinc. Special brasses and bronzes may contain other metals.

Copper, silver, and gold are soft and malleable, a property that made their early use possible, for they could be hammered into vessels and ornaments with stones. Gold is the most malleable of all metals. All three are inactive enough to occur in the free state, another characteristic that led to their early use.

Of the three, copper is the most important because of its wide use as an electrical conductor. Actually, silver excels copper in this property but is too scarce to supply the demand. Other uses for copper include the manufacture of such building materials as roofing and gutters, and the making of alloys.

Silver and gold ornaments, coins, jewelry, and tableware are frequently alloys of silver and copper, gold and copper, or gold and silver. For example, 12-carat solid yellow gold is 50 per cent copper (24 carat is pure gold). These alloys are generally harder and more durable than pure silver and pure gold.

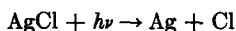
**Mirrors.** The reflecting surface of an ordinary mirror is silver. The silver is plated out on the glass from a silver nitrate-ammonia solution by the reduction of the silver ions with a mild reducing agent, such as glucose or formaldehyde. These two substances can be considered as sources of hydrogen that is oxidized to hydrogen ion:



**Photography.** Silver bromide, AgBr, is the light-sensitive compound that is responsible for the production of black-and-white or natural-color photographs and motion pictures, and color transparencies. The silver bromide, a cream-white solid, is dispersed in gelatin, and the mixture is spread on transparent cellulose acetate to make film, or on paper to make photographic paper. Silver chloride and silver iodide may also be used for special-purpose films and papers. When these compounds are exposed to light, the ions absorb radiant energy and become much more susceptible to chemical reduction by

mild reducing agents (*developers*). Black colloidal silver is formed in the gelatin in varying amounts to form a negative of the image.

**PHOTOCHROMIC GLASS.** A recently discovered use of the photochemical reduction of silver halides is in making glass which is light-sensitive but which darkens and lightens reversibly, depending on the amount of radiation it is being exposed to. Colloid-sized crystals of silver halides embedded in glass decompose when exposed to light and cause the glass to darken; for example,



The Ag and Cl atoms, trapped in the glass, cannot diffuse away from each other, so that they recombine quickly. In the absence of light the atoms combine completely to form silver chloride, and the glass regains its original transparency. This type of glass promises to be useful for windows and eye glasses that will darken to keep out glare during the day but will become transparent again at night.

## **ZINC, CADMIUM, AND MERCURY**

Unlike the alkali and alkaline earth metals (groups IA and IIA), which become more active as the atomic weight increases, the members of the copper and zinc families (IB and IIB) become less active. Gold and mercury are the least active in their respective families. Zinc and cadmium are the only metals in these two families that are more active than hydrogen in forming positive ions.

The most extensive use of zinc is in the production of *galvanized iron*, that is, iron coated with a thin layer of zinc to protect against corrosion. Galvanized iron products include roofing, gutters, tubs, pails, water pipes, tanks, and wire fences. (The protective action of zinc was discussed in Chap. 19, in connection with corrosion.)

Some of the important uses of mercury—for example, in barometers, thermometers, electrical devices, and mercury vapor lamps—depend in part on its low melting and boiling points. Alloys of mercury are called **amalgams**; those of tin, silver, and gold are used for metallic fillings in teeth. The tendency of mercury to alloy at room temperature has led to its use in *amalgamation*, a process for recovering gold and silver from native ores. A great deal of mercury is used in an electrochemical method of producing chlorine and sodium hydroxide. Mercury compounds, which are often poisonous, are used in fungicides and pharmaceuticals. Approximately 2,000 tons of mercury is used per year in this country.

The annual production of cadmium in the United States is not high, about 5,000 tons. Cadmium is a component of some low-melting alloys that are used as electrical fuses, in automatic fire-sprinkling systems, and as safety plugs in steam boilers. It is also used as a coating for iron and other metals to increase corrosion resistance.

## **TIN AND LEAD**

Tin is most familiar to us as tin cans, an invention that has had a profound influence on man's habits. Actually, a tin can is an iron can that is covered with a thin coat of tin that protects the iron against corrosion, particularly that caused by organic acids in foods.

The tin is plated on the iron by dipping sheet iron (cleaned by pickling in an acid bath) into molten tin or by electroplating. Between one-third and one-half of the tin used in the United States (about 60,000 tons annually) goes into the production of tin plate.

Once the tin coating is broken, the iron corrodes more rapidly than it does if not plated with tin. This is because iron is more active than tin and hence undergoes oxidation in the electrochemical cells formed when tin and iron are exposed to the same solution. Iron forms the supporting structure; therefore, once corrosion starts, holes appear rapidly in the can. The reverse is true of galvanized iron. Zinc, being more active than iron, undergoes oxidation in the electrochemical cells involved here. The zinc must be corroded from a considerable area before the supporting iron structure is much affected.

Large amounts of lead are used in plumbing and in lead storage batteries (Chap. 18), and both lead and tin are widely used in alloys (see Table 20-4).

## **PLATINUM METALS**

The platinum metals are useful chiefly because of their chemical inertness. Platinum, for example, is used as the spinneret in the production of rayon (see Chap. 28), because it resists the corrosive action of the basic sodium hydroxide solution on one side of it and the sulfuric acid solution on the other. Platinum vessels and platinum stirrers are used in the melting of optical glass. Expensive fountain pen points and permanent phonograph needles may be tipped with an osmium-ruthenium alloy that is extremely hard and very resistant to corrosion. The widespread use of platinum and palladium in jewelry obviously depends in part on the chemical durability of these metals. In addition to the uses already mentioned, platinum and palladium are important as catalysts in the production of certain chemicals and drugs and as breaker points in electrical circuits, where high resistance toward wear and spark erosion is required. The electrical industry uses over half of the platinum metals consumed in this country. Platinum is well suited for making certain scientific apparatus, such as electrodes for precise work and unreactive crucibles.

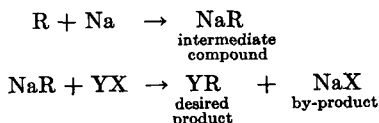
## **METALLO-ACID METALS**

Except for chromium, the metallo-acid metals (Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, and Re) are among the more unfamiliar metals; chromium is familiar to all as chromium plate on automobiles,

plumbing fixtures, etc. Nevertheless, these metals play an important part in a country's industrial life, for they are essential to many of the special alloy steels required for the manufacture of machinery of all kinds (Table 20-3). In addition, some of the metals have important applications other than in alloys. Tungsten, for example, is used for filaments in electric light bulbs, electrodes in neon tubes, targets for X-ray tubes, and contact points for electrical devices. Molybdenum, rhenium, and tantalum can be used for many of these same purposes. Rhenium, last of the naturally occurring, nonradioactive elements to be discovered (1925), is produced as a by-product from copper smelter flue dust.

## METALS OF GROUPS IA AND IIA

**Sodium.** Many thousands of tons of sodium is used each year in the synthesis of lead tetraethyl,  $\text{Pb}(\text{C}_2\text{H}_5)_4$ , the most widely used anti-knock agent for gasoline, and in the synthesis of dyes, medicines, and other organic chemicals. In these processes, the sodium does not become part of the desired product. Neither does it act as a catalyst, because the reaction proceeds in a manner that converts the sodium into a stable and usually worthless compound that cannot be used again economically. The role the sodium plays may be summarized in this way. One of the reactants combines with the sodium to form a very active intermediate compound, which then combines with the second reactant to produce the desired product and a by-product sodium compound (frequently sodium chloride):



Sodium is also used in the production of sodium peroxide and sodium cyanide, and in sodium vapor lamps. Because molten sodium is an excellent conductor of heat, valves of internal-combustion engines are sometimes filled with it to aid in conducting the heat away from these parts. It is also used as a heat transfer medium in nuclear reactors (see Chap. 15).

**Cesium and Rubidium.** Cesium and rubidium are used in photoelectric cells, because of their low ionization energies (see Fig. 20-9). Based also on this property is the prospective use of cesium as a propellant for space vehicles. In one model "ion engine," cesium atoms are ionized, accelerated to high velocities by electrodes, neutralized to atoms, and expelled as a thrust-producing blast of gas from the rear of the engine.

**Beryllium.** Beryllium is used in small amounts in alloys. A small percentage added to gold makes the gold harder; a little added to

## METALS: NATURAL SOURCES, PRODUCTION, AND USES

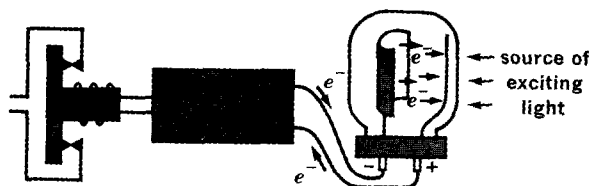


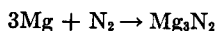
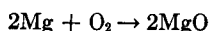
FIG. 20-9

Diagram of a photoelectric cell. A curved metal foil is coated with an active metal such as rubidium or cesium. When light strikes the active metal, its atoms emit electrons. Therefore, as long as a light shines into the tube, a current will flow through it. This current is so weak that it must be amplified to make it strong enough to turn on an electric switch or do other useful work.

nickel makes the metal much stronger; added to copper, it makes an alloy that is especially suited for springs because of its remarkable elasticity and resistance to breaking after prolonged flexing.

**Magnesium.** Magnesium is the only one of these metals that is important as a structural material; it is the chief component in a number of strong, low-density alloys used in airplane, rocket, and satellite construction. Increasingly, magnesium is used in all sorts of vehicles and other construction where minimum weight is economical or convenient.

Magnesium powder or ribbon is used in some photoflash bulbs and in incendiary bombs. A magnesium-barium alloy is used as a degassing agent for evacuated electronic tubes. This use is based on the activity of hot magnesium (and barium) toward both of the main constituents of air, oxygen and nitrogen:



The formation of the solid oxide and nitride removes traces of the two gases that would otherwise remain and interfere with the operation of the tube.

## CHAPTER REVIEW

### Topics

Minerals, ores, igneous rock, sedimentary rock, metallurgy, gangue, flux, slag, smelting, blast furnace, pig iron, cast iron, steel, open-hearth furnace, hematite, magnetite, bauxite, alloy, galvanized iron, amalgams.

### Exercises

1. Many scarce metals are fairly well known and widely used, whereas some that are much more common in minerals are not known to the general public. Why?

2. Which are more numerous in the earth's crust, sodium or calcium atoms?
3. The mineral *barite*, chiefly barium sulfate, could be found exposed anywhere, whereas the mineral *epsomite*, chiefly magnesium sulfate, would be found only below the surface in most localities. Why?
4. An incendiary bomb containing magnesium is not effectively put out with water but must be covered with dirt if possible. Why?
5.
  - a. Scandium is much more common in the earth's crust than is silver; yet silver has been known and used for much longer. Why?
  - b. Palladium is slightly more common on the earth's crust than silver; yet the latter is more widely used and is cheaper. Why?
6. List several metals that are found in nature as atoms; as cations; as, or in, anions.
7. Explain why the elements in misch metal should be so alike physically and chemically.
8. Suppose one were given six vials said to contain solid samples of the following:  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{FeS}_2$ ,  $\text{Cu}_2\text{S}$ , and  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ . Describe simple chemical and physical tests, other than simple physical properties, by which one could identify the substances.
9. If a recently discovered Canadian iron ore deposit (69 per cent iron) is practically a pure compound, what must it be? What would be another way of accounting for the percentage composition only?
10. What are some useful by-products of the copper industry?
11. Suppose that lead chloride, silver chloride, and sodium chloride were deposited as the result of the evaporation of a single salt lake. Describe the sediment that might be left behind; predict its homogeneity or heterogeneity on the basis of data.
12. How could you probably distinguish, on the basis of a simple test with hydrochloric acid, between a sulfide, a carbonate, and a silicate ore?
13. Explain how it is possible for the geologist to find valuable ores by examining plant life.
14. Describe the common methods of removing gangue. Which were probably not used by gold prospectors in the Old West?
15. Write equations for five specific instances that illustrate the generalization that the first chemical step in winning a metal from its ore is usually a reduction reaction.
16. Suggest a way to recover metallic silver from the ore  $\text{Ag}_2\text{S}$ . Write equations for any chemical steps.
17. Iron rusts easily, whereas cobalt and nickel do not. Suggest an explanation for this.
18. Write the equation for the reduction of titanium chloride with magnesium. Could aluminum chloride be effectively reduced in a similar manner?



**METALS: NATURAL SOURCES,  
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19. What are the coinage metals? Which one would an industrial nation miss most if it could get no more of it? Justify your choice.
20. In discussing the electrolytic purification of copper, impurities were divided into four groups. Describe in general terms how these groups differ from one another. Considering that a copper purification cell may be used for a long period of time, describe how each group of impurities is separated from the copper and removed from the cell.
21. In the electrolytic refining of copper, why it is undesirable to let the voltage become too high; too low?
22. Consider a small particle of limestone dropped into a blast furnace. Write equations for all the possible reactions that it or its products undergo while in the furnace.
23. To produce iron economically, a plant should be located within as short a distance as possible of what three principal raw materials?
24. Using data from Chap. 16 and Table 1 of the Appendix, calculate the fuel value, in Btu/ft<sup>3</sup> at 25° and 1 atm, of a blast furnace flue gas that is 12 per cent by volume CO, 1 per cent H<sub>2</sub>, and the rest nitrogen and carbon dioxide. Compare your answer with the values given for fuel gases in Table 24-3.
25. An ore contains 3.2 per cent calcium carbonate after flotation treatment. What is the theoretical weight of sand needed per ton of ore for slag formation? What weight of slag would be formed?
26. The early steel producers were greatly concerned with the loss of so much CO in the flue gas from the blast furnace. To increase the extent to which the CO was used in reducing Fe<sub>2</sub>O<sub>3</sub>, they built taller, more expensive furnaces. But the percentage of CO in the escaping gas remained about the same. Suggest a reason for this.
27. Describe some of the differences between cast iron and steel.
28. In the production of blast furnace iron, which raw material is used in the greatest amount by weight?
29. Write equations for possible slag-forming reactions in the removal of sulfur and phosphorus oxides from steel in the open-hearth process.
30. What weight of ore would be necessary to prepare a ton of iron if the ore were 90 per cent hematite and the overall process were 85 per cent efficient?
31. Compare the Bessemer and open-hearth processes as to (a) the removal of excess carbon from blast-furnace iron, (b) the quality of the steel produced, and (c) control over percentage composition of alloy elements.
32. Could aluminum ingots be purified in a manner similar to that used for copper? Explain by means of equations and a discussion.
33. Discuss the economic location of an aluminum plant in terms of needed raw materials and other requirements.
34. What is the cost of electrical energy for producing a pound of aluminum if the current is delivered at 6.0 volts at a rate of 0.35 cent per kilowatt-hour?

35. List several oxide ores for which carbon might be used as a reducing agent and several for which it could not.
36. Would the reaction  $2\text{NaCl} \rightarrow 2\text{Na} + \text{Cl}_2$  occur simply on heating to a high enough temperature? If so, what justifies the use of the electrolytic method of decomposition?
37. Consider the data in Table 29-3 and the  $K_{sp}$  of  $\text{Mg}(\text{OH})_2$  as given in Table 3 of the Appendix. Calculate the approximate lower limit for the  $K_{sp}$  of  $\text{Ca}(\text{OH})_2$  in the light of the use of lime to precipitate magnesium hydroxide from sea water. Assume that 90 per cent of the  $\text{Mg}^{2+}$  is precipitated and that the density of sea water is unity.
38. Suggest a theoretical explanation, based on bonding and structure, for the fact that many mechanically strong alloys can be formed (from two or more elements) that vary in composition practically without limit.
39. List some of the elements that are in most steels and some that are present in special steels.
40.
  - a. List four properties that might make an alloy more useful than a pure metal.
  - b. For what uses might a pure metal be preferred to an alloy?
41. What properties would be desirable in an alloy used to sheath the capsules that have carried astronauts? To what laboratory tests might alloys be subjected to evaluate them for this use?
42. Describe the essential chemistry involved in black-and-white photography, from the exposure of the film to the production of a negative.
43. By means of diagrams and equations explain the difference in corrosion characteristics of iron protected by a broken zinc coating and iron protected by a broken tin coating.
44. Rhenium, the last nonradioactive element to be discovered, was sought avidly by many chemists before it was isolated and identified in 1925. Where might they have looked for the missing element? How might they have proved the material they isolated was an element and different from any other element?
45. In the light from sodium vapor lamps, colored objects tend to look black or gray, sometimes yellowish. Explain.
46. Draw a diagram to illustrate the principle of operation of a cesium-ion engine for a space ship.
47. Account for the following:
  - a. A much higher proportion of copper is produced in high purity than is iron.
  - b. In flotation separation, often the less dense of two substances settles to the bottom of the separation vessel.
  - c. Copper has been used for much longer than chromium, although the latter also resists corrosion and is more common in the earth's crust.
  - d. Aluminum has greater electrical resistance than copper; yet the former is replacing the latter for many high-capacity electrical cables.

**METALS: NATURAL SOURCES,  
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- e. Rhenium is used for contact points in some electrical switches and for filaments in certain incandescent bulbs.
- f. Rubidium rather than rhodium is used in photoelectric cells.

**SUPPLEMENTARY READING**

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**GROUP VIIA:****THE HALOGEN FAMILY**

We began our study of families of elements at the left of the periodic table with groups IA and IIA and then had a brief look at a great number of other metals. In this chapter we go to the right of the table to pick our first family of nonmetals, group VIIA. As mentioned earlier, family resemblances are strongest in the groups at the far left and far right of the periodic table; in group VIIA the elements are indeed quite similar to one another, which makes their study somewhat easier than for other nonmetal groups.

**PROPERTIES OF THE HALOGEN FAMILY**

The elements fluorine, chlorine, bromine, and iodine were known as the *halogen family* of elements long before the formulation of the modern atomic theory that groups them together in the periodic table. However, the similarities of these elements are best explained and studied against the background of their atomic structure. Each element in family VIIA has seven electrons ( $s^2p^5$ ) in its outside main energy level. In addition to the four common elements, there is a rare halogen, astatine, which has been known since 1940, when it was made by means of nuclear bombardment experiments. Since then it has been found to occur in nature, but only in extremely minute quantities.

**PHYSICAL PROPERTIES**

Table 21-1 lists some of the important physical properties of the halogens; some others are listed in Table 16-5. The striking generality evident from the tabulated data is that any given property changes in a regular way from one element to the next.

**GROUP VIIA:  
THE HALOGEN FAMILY**

**TABLE 21-1**     *Physical properties of the halogen family*

	fluorine F	chlorine Cl	bromine Br	iodine I
appearance at room temperature	yellowish gas	greenish gas	deep red liquid	purple, almost black, solid
molecular formula	F <sub>2</sub>	Cl <sub>2</sub>	Br <sub>2</sub>	I <sub>2</sub>
melting point, °C	-218	-101	-7	114
boiling point, °C	-188	-34	59	184
ionization energy, ev	17.34 (400 kcal)	12.95 (299 kcal)	11.80 (272 kcal)	10.6 (244 kcal)
radius of atom, A	0.72	0.99	1.14	1.33
radius of ion (X <sup>-</sup> ), A	1.36	1.81	1.95	2.16
electronic structure	2,7	2,8,7	2,8,18,7	2,8,18,18,7
electronegativity	4.0	3.0	2.8	2.5

The increase in melting and boiling points with atomic number is explained by the fact that larger molecules have greater masses and greater intermolecular attraction than do small ones. The I<sub>2</sub> molecules have the greatest number of electrons far away from their respective atomic nuclei; and because these electrons are attracted by the nuclei of other iodine atoms, the van der Waals forces in iodine are stronger than in the smaller molecules of the other halogens.

Except for the noble gases, the halogens have the highest ionization energies of any family of elements. These high values are associated with the nearly complete *p* sublevels, as pointed out in the discussion of orbitals and ionization energies in Chap. 3. The trend in ionization energies in group VIIA reveals that the fluorine atom holds most tightly to its electrons, the iodine least tightly. This trend may be correlated with the sizes of the halogen atoms by referring to Fig. 21-1.

  
F 0.72 A

  
Cl 0.99

  
Br 1.14

  
I 1.33

**FIG. 21-1**

Relative sizes of halogen atoms.

### CHEMICAL PROPERTIES

All four elements are extremely irritating to the nose and throat, although the low vapor pressure of solid iodine prevents high concentrations of it in the air. Liquid bromine is one of the most dangerous of the common laboratory reagents, because of its effect on the eyes and nasal passages and because it causes severe burns on contact with the skin. Chlorine and fluorine, usually handled as gases, should be used only in hoods and in rooms with good ventilation. All the halogens must be kept out of contact with substances that can be oxidized.

There is a regular decrease in chemical activity from fluorine to iodine, as shown by the trend in oxidizing strengths. The trend in standard oxidation potentials (Table 18-1) should also be noted. The

diatomic fluorine molecule,  $F_2$ , is a stronger oxidizing agent than any other element in its normal state. A look back at Table 16-5 shows that this statement requires explanation, because the chlorine atom has a higher electron affinity than the fluorine. However, when we think of different diatomic molecules acting as oxidizing agents, we realize that two steps are important: (1) the dissociation of the molecules into atoms and (2) the winning of electrons by the individual atoms. The total enthalpy change,  $\frac{1}{2}\Delta H_{dis} - \Delta H_{ea}$ , will determine which molecule is the stronger oxidizing agent:



From the data in Table 16-5, these sums are:

For F:  $18.3 - 81.0 = -62.7 \text{ kcal/mole}$

For Cl:  $29.0 - 87.1 = -58.1 \text{ kcal/mole}$

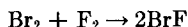
The sums for bromine and iodine atoms are  $-54.0$  and  $-48.0 \text{ kcal/mole}$ , respectively.

For each of the halogens, the dissociation of the diatomic molecule plus the gaining of electrons by the atoms is exothermic overall. For fluorine the overall change is most exothermic, and fluorine is correspondingly the most active oxidizing agent.

Both fluorine and chlorine support combustion reactions in the same manner as does oxygen. Hydrogen and the active metals burn in either gas with the liberation of heat and light.

**Principal Reactions.** Here we list some of the reactions of halogens with other substances that are of considerable importance in industry or research and hence are of interest. In these reactions the symbol X is sometimes used in formulas to indicate any halogen.

**HALOGENS WITH HALOGENS.** In a reaction between two halogens, the one with the lower atomic number will be the oxidizing agent and will be assigned a negative oxidation state in the compound. Consider the reaction of bromine with fluorine:



Although the bond is largely covalent (no discrete ions are formed), the electron pair is drawn over toward the fluorine ( $\delta^-$ ) and away from the bromine ( $\delta^+$ ). The molecule is polar.

Many interhalogen compounds are known, the fluorides being most common. In the fluorides the possible number of fluorine atoms per molecule increases from chlorine to iodine, for example,  $ClF_3$ ,  $BrF_5$ , and  $IF_7$ . Interhalogen compounds are very active oxidizing agents, behaving chemically much like mixtures of halogens.

The structures of interhalogen molecules and ions can often be explained in terms of *hybrid orbitals*, as mentioned in that section in

GROUP VIIA:  
THE HALOGEN FAMILY

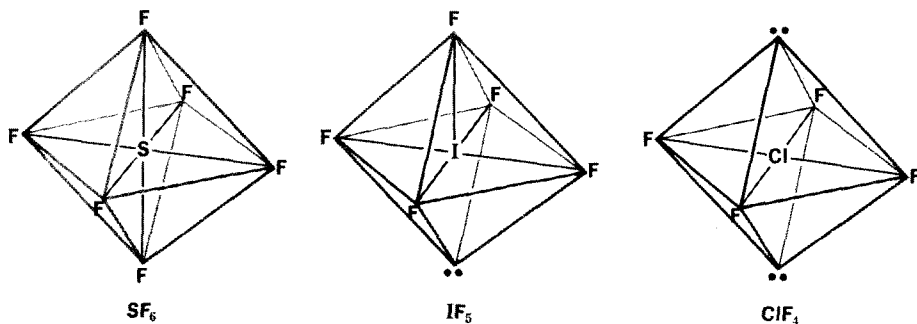
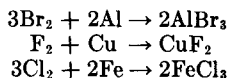


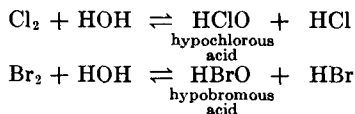
FIG. 21-2 Typical fluorides which have octahedral, hybrid-bond symmetry. In the two interhalogen structures, positions at apexes of imaginary octahedra are taken by unshared pairs of electrons.

Chap. 17. It would not be predicted on the basis of their simple formulas, but  $IF_5$  and  $ClF_4^-$  have structures that can be related to octahedra, as shown in Fig. 21-2, where they are compared with  $SF_6$ .

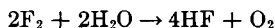
WITH METALS. The halogens react readily with most metals. Bromine and iodine do not react with gold, platinum, or some of the other noble metals, but fluorine and chlorine attack even these inactive elements. Examples:



WITH WATER

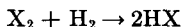


Fluorine gives hydrofluoric acid but no hypofluorous acid:



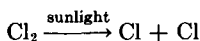
Solutions of chlorine or bromine in water are strong oxidizing agents. In these solutions  $HClO$  or  $HBrO$  usually functions as the oxidizing agent. The bleaching action of chlorine is accounted for on the assumption that chlorine first reacts with water to form hypochlorous acid ( $HClO$ ), which then oxidizes colored compounds to colorless ones. In the compound  $HXO$ ,  $X$  has an oxidation state of +1 and has a strong attraction for one or two electrons.

WITH HYDROGEN

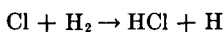


The reaction takes place with explosive violence for fluorine and even chlorine, but bromine and iodine react slowly. (See hydrogen halides, page 574.)

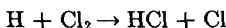
The reactions are said to be **photochemical**, because they occur much more rapidly on exposure to radiant energy. A mixture of hydrogen and chlorine can be kept in the dark for a long time, but when the mixture is exposed to sunlight a violent combustion occurs. The sunlight causes some of the chlorine molecules to dissociate into (very active) atoms of chlorine. The minimum energy for this decomposition is possessed by photons of  $4.9 \times 10^{-5}$  cm or 4,900 Å wavelength (see Chap. 17):



The chlorine atoms can then react with hydrogen molecules to form hydrogen chloride and (active) hydrogen atoms:

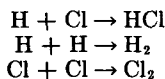


Next, hydrogen atoms can react with other chlorine molecules. Note that a chlorine atom is again formed:

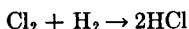


This is a **chain reaction**. Presumably there are relatively few atoms of hydrogen and chlorine in existence at any one time; but as the reaction proceeds, additional atoms are successively formed in the manner indicated by the equations above.

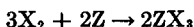
The chain is broken (1) when atoms of chlorine react with atoms of hydrogen, or (2) when atoms of hydrogen react with one another, or (3) when atoms of chlorine react with one another:



The breaking of the chain tends to stop the reaction between the hydrogen and chlorine. However, all three reactions liberate heat; hence, if the temperature rises sufficiently, hydrogen and chlorine molecules will react. The reaction, which eventually goes to completion, is written simply as

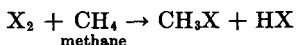


WITH CERTAIN NONMETALS (Z)



Z can be B, P, or As.

WITH COMPOUNDS OF CARBON AND HYDROGEN



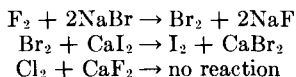
This very important type of reaction is discussed in detail in Chap. 26.

WITH COMPOUNDS OF OTHER HALOGENS. This type of reaction can be thought of simply as a displacement reaction, with the more



**GROUP VIIA:**  
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active halogen displacing a less active one from its compounds.  
Examples:



**OCCURRENCE**

Although traces of elemental iodine have been found in nature, the halogens are chemically too active as electron acceptors to exist as free elements in this world of ours, comprised as it is of the other common atoms, ions, and molecules. Like other active elements, the halogens exist in nature primarily in compounds. Their most common state is as the halide ions  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ . These ions always occur in association with positive ions (compounds). Because the compounds of the halides are usually soluble in water, the halide ions are found concentrated in the sea, in salt lakes, and in underground beds of salt that were formed ages ago by the evaporation of bodies of salt water.

Listing them in order of their abundance in the earth's crust gives Cl, 0.2 per cent, F, 0.1 per cent, and Br and I, 0.001 per cent each. Because the halogens, taken together, comprise about 3 out of every 1,000 lb of the earth's crust, they are rather common elements. Some of the abundant halogen-containing minerals are listed in Table 21-2. Sodium chloride is one of the most important of all inorganic raw materials. Not only is it used as salt, but it is the starting material for the commercial manufacture of most sodium and chlorine compounds. Bromine is produced commercially from sea water; iodine is found concentrated in sea weed, although sodium iodate is the chief commercial raw material.

The halogens have important roles in the chemical reactions of our bodies. Traces of chloride ion are found in ordinary drinking water. Chloride is one of the essential ions in the blood and gastric juices. Iodide ion is usually present in water in minute amounts. In localities where it is not present, the prevalence of goiter, a condition of the thyroid gland, is increased. Iodide ion tends to concentrate in the thyroid gland and in certain other human tissues. Traces of fluoride ion in drinking water are effective in preventing tooth decay, but too much fluoride may cause the teeth to be mottled or chalky.

**PREPARATION AND USE OF THE HALOGENS**

The halogens can be prepared by suitable chemical or electrochemical procedures from naturally occurring compounds. In most cases the chemical change that is involved results in electrons being taken away from a halide ion. That is, an oxidation reaction must be brought about. In the case of chloride, bromide, and iodide ions there are strong chemical oxidizers that are effective, but the electronegativ-

*Abundant halogen-containing minerals*

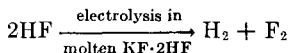
TABLE 21-2

formula	chemical name	mineral name
$\text{CaF}_2$	calcium fluoride	fluorspar
$\text{Na}_3\text{AlF}_6$	sodium aluminum fluoride	cryolite
$\text{NaCl}$	sodium chloride	halite
$\text{KCl}$	potassium chloride	sylvite
$\text{KCl}$ and $\text{NaCl}$	potassium and sodium chloride	sylvinite
$\text{MgBr}_2 \cdot \text{KBr} \cdot 6\text{H}_2\text{O}$	magnesium potassium bromide	bromo-carnallite
$\text{NaIO}_3$	sodium iodate	
$\text{NaIO}_4$	sodium periodate	

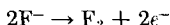
ity of the fluorine atom is so high that chemical oxidizing agents are ineffective. The common way to produce fluorine is by electrolysis.

**FLUORINE**

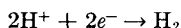
The commercial source of fluorine is the mineral fluorspar,  $\text{CaF}_2$ . By treating the calcium fluoride with sulfuric acid, hydrogen fluoride is produced (see page 576). Elemental fluorine is produced by the electrolytic decomposition of hydrogen fluoride:



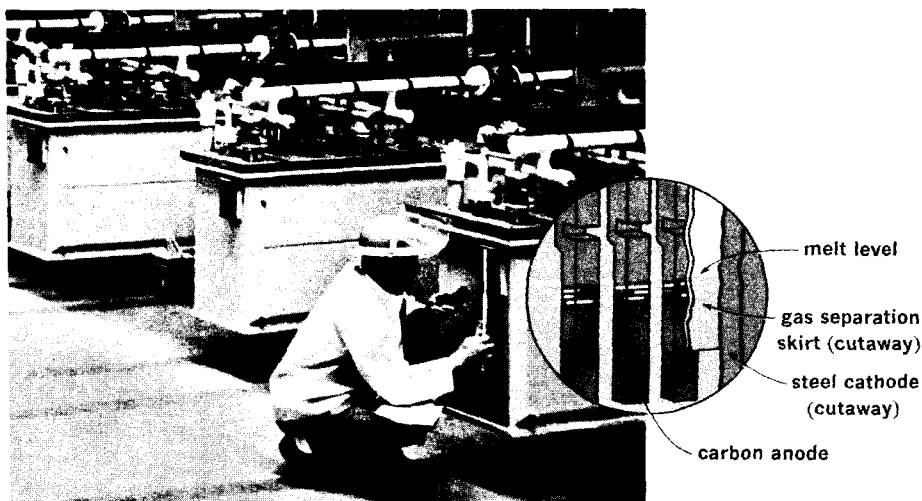
Oxidation at the anode:



Reduction at the cathode:



A view of industrial cells for fluorine production is shown in Fig. 21-3.



Interior view of a fluorine plant showing electrolysis cells. The cutaway drawing shows the carbon anodes and steel cathodes. (Courtesy of Allied Chemical Corporation.)

FIG. 21-3

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The direct electrolysis of liquid HF is not practical, because this compound is a nonelectrolyte. A solution of HF in molten  $\text{KF} \cdot 2\text{HF}$  at 80 to 100° forms a conducting solution that can be electrolyzed to yield hydrogen and fluorine. HF must be added to the molten salt bath continually to replace the HF that is being decomposed.

The electrolysis is carried out under strictly *anhydrous* conditions, that is, no moisture. The  $\text{F}^-$  ion cannot be oxidized in the presence of water, because the  $\text{OH}^-$  ion gives up an electron more easily than the  $\text{F}^-$  ion does.

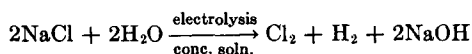
**IMPORTANCE OF FLUORINE PRODUCTION.** Elemental fluorine is needed in the manufacture of many useful compounds, among which are the Freon refrigerant gases, such as  $\text{CCl}_2\text{F}_2$ , and the heat-resistant plastic Teflon. Fluorine plays a key role in the nuclear energy field, being used to make uranium hexafluoride,  $\text{UF}_6$ , the volatile uranium compound used in the gaseous diffusion method of separating the  $^{235}\text{U}$  and  $^{238}\text{U}$  isotopes.

Liquid fluorine has been used as oxidizing agent in some rockets. Very high energy yields per pound of propellant are obtained when fluorine acts as the oxidant.

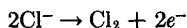
## CHLORINE

**Commercial Preparation.** Chlorine, to the extent of about 6 million tons annually in the United States, is produced commercially in several ways. We shall describe two important electrolytic processes.

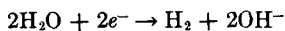
The first method is by the electrolysis of a concentrated sodium chloride solution with unreactive electrodes. The following reactions occur:



Oxidation at the anode:

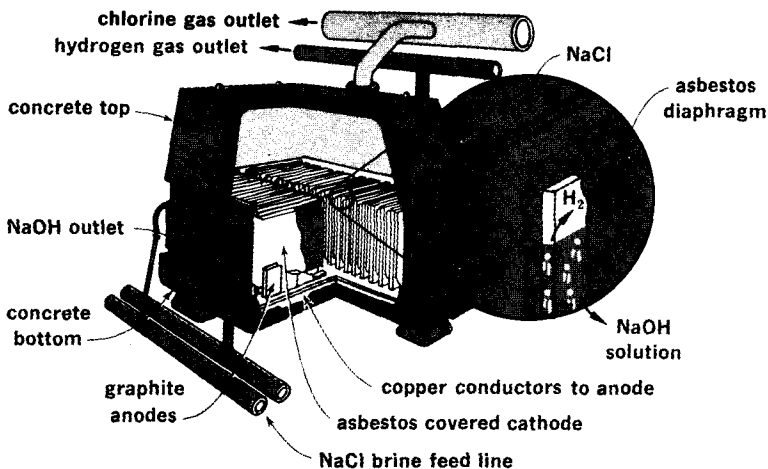


Reduction at the cathode:



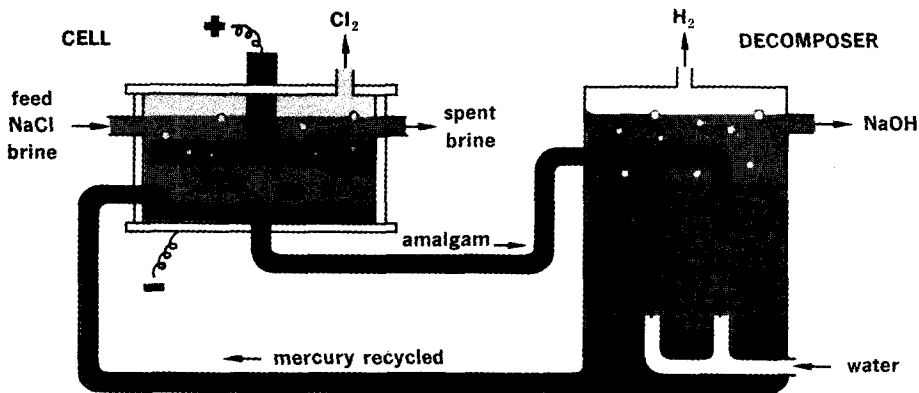
These reactions can be carried out in equipment like that shown in Fig. 21-4. Major problems are to keep the chlorine and hydrogen gases separated, because they react explosively, and to keep the chlorine away from the sodium hydroxide solution, because they will also react. These separations are achieved by use of an asbestos cloth diaphragm through which solutions can pass en route to electrodes but which, when wet, stops gas bubbles. Hydrogen gas and sodium hydroxide solution are formed at the cathodes on one side of the diaphragms and are taken out of the cell via side and bottom conduits;

GROUP VIIA:  
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An electrolysis cell for the production of chlorine. (Redrawn by courtesy of Hooker Chemical Corporation.)

FIG. 21-4



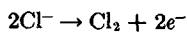
Another type of cell for the production of chlorine by electrolysis of brine. (Redrawn by courtesy of the Olin Mathieson Chemical Corporation.)

FIG. 21-5

chlorine gas, formed on the opposite side of the diaphragms at the anodes, is taken out of the top of the cell.

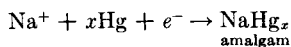
The second method also involves the electrolysis of concentrated sodium chloride, but liquid mercury is used as the cathode (Fig. 21-5). Because sodium dissolves in mercury to form sodium amalgam,  $\text{NaHg}_x$ , this provides an ingenious way of producing the hydrogen and sodium hydroxide in an entirely separate vessel from the chlorine. The reactions in the primary electrolysis are:

Oxidation at the anode:

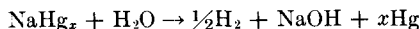


GROUP VIIA:  
THE HALOGEN FAMILY

Reduction at the cathode:



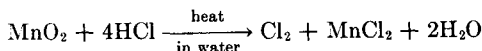
The liquid amalgam is then pumped into a decomposing vessel where it reacts with water to produce hydrogen and sodium hydroxide solution:



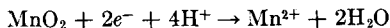
The mercury is pumped back to the electrolysis cell for re-use.

Both these processes are continuous, with fresh brine flowing into the cells and the three products,  $\text{Cl}_2$ ,  $\text{H}_2$ , and  $\text{NaOH}$  solution, flowing out. Hundreds of large cells are commonly used in a single plant. Individual cells are shut down as needed for cleaning and replacing worn electrodes, especially the anodes, which are attacked by the chlorine.

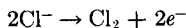
**Laboratory Preparation.** The laboratory preparation of chlorine can be carried out in a variety of ways, practically all of which involve the oxidation of the chloride ion. We shall describe two of these procedures. First,



Manganese in the +4 oxidation state is a strong oxidizing agent. The reduction reaction



takes place as the  $\text{Mn}^{4+}$  acquires  $2e^-$  from two  $\text{Cl}^-$  ions (the latter is the oxidation reaction):

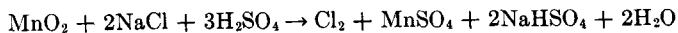


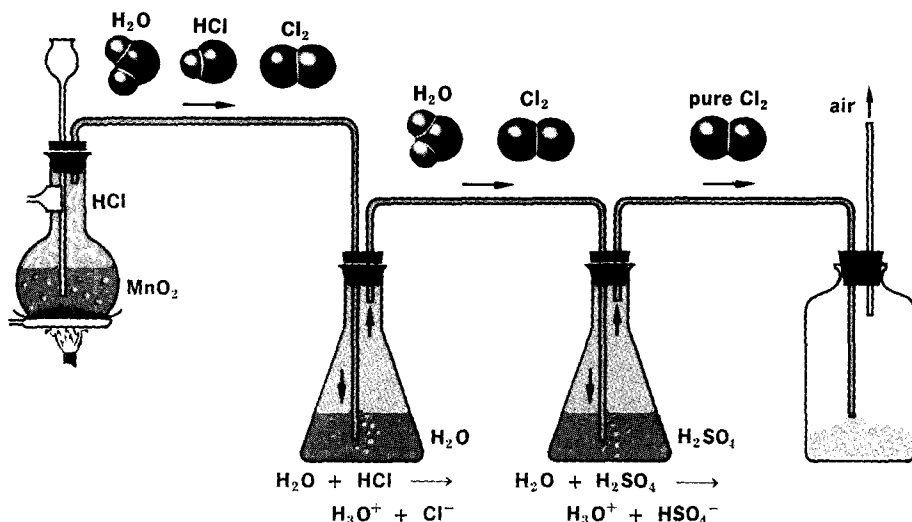
If needed, the solution is heated slightly to speed up the reaction and to force the  $\text{Cl}_2$  out of solution (see Fig. 21-6). The reaction is carried out in an acid solution so that  $\text{H}^+$  ions will be available to combine with the  $\text{O}^{2-}$  ions, which are initially associated with  $\text{Mn}^{4+}$  ions.

The gas is bubbled through cool water to be stripped of any  $\text{HCl}$  contaminant; then the wet  $\text{Cl}_2$  is bubbled through concentrated sulfuric acid to be stripped of the water vapor.

Historically, this is the reaction investigated by Wilhelm Scheele in 1774, when he discovered chlorine. It is still used for preparing small quantities of  $\text{Cl}_2$  gas from easily available chemicals.

For a second laboratory procedure, we note that the source of  $\text{Cl}^-$  need not be hydrogen chloride; it can be a salt containing the chloride ion. The reaction is carried out in an acid solution. For example:

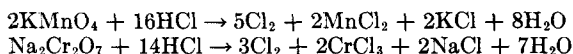




Laboratory preparation of chlorine. The dense chlorine displaces air.

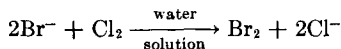
FIG. 21-6

Several different oxidizing agents can be used to attract electrons from the chloride ion and cause the formation of elemental chlorine. Examples of such agents are permanganates and dichromates:

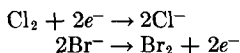


## BROMINE

**Commercial Preparation.** Our most abundant sources of bromine compounds are brines from salt wells and from the ocean. Because water from these sources usually contains large proportions of chloride ions in comparison with the amount of bromide ions, the preparation of bromine must involve an oxidizing agent that does not simultaneously oxidize chloride ions. Chlorine itself is admirably suited for this job:



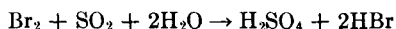
The chloride ion has a greater electron affinity than the bromide ion:



When ocean water, which is slightly alkaline, is the raw material, the water is first made acidic, to prevent the reaction of the chlorine gas with  $\text{OH}^-$  ions. The water is then pumped into towers as a spray, where it comes in contact with chlorine gas. The bromine that forms in these towers is blown out into another chamber by a blast of air.

**GROUP VIIA:**  
**THE HALOGEN FAMILY**

To separate the bromine from the large volume of air, the proper amount of sulfur dioxide is added to the mixture. The reaction is as follows:

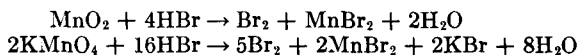


The hydrogen bromide (and sulfuric acid) are removed from the air with water, to make a fairly concentrated solution of hydrogen bromide. Treatment of the solution with chlorine again frees the bromine, this time in a concentrated form. This involved process is necessary, because huge quantities of ocean water must be processed to obtain a small amount of bromine (sea water contains 67 parts per million).

**IMPORTANCE OF BROMINE PRODUCTION.** A large part of the 100,000 tons of bromine produced yearly in this country is used to produce ethylene dibromide,  $\text{C}_2\text{H}_4\text{Br}_2$ , a component of Ethyl gasoline. The compounds lead tetraethyl and lead tetramethyl are present in Ethyl gasoline as antiknock agents, but the lead formed during their combustion tends to foul the spark plugs. Consequently ethylene dibromide is also added to the gasoline so that the compound lead bromide will be formed during combustion. Lead bromide is volatile and escapes with the exhaust gases.

A great amount of bromine is used in the manufacture of silver bromide, one of the light-sensitive compounds of photographic film and paper. Certain bromine compounds are also used in medicines.

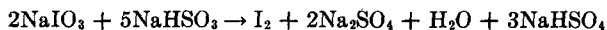
**Laboratory Preparation.** Any of the reactions used for the preparation of chlorine can be modified for preparing bromine; for example:



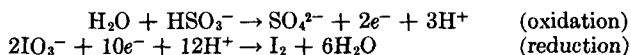
## **IODINE**

Methods used in preparing chlorine can be used to prepare iodine if the element is present as the iodide ion. The cheapest source, however, is the compound sodium iodate,  $\text{NaIO}_3$ , which is found associated with large deposits of sodium nitrate in Chile.

### **Commercial Preparation**



The sulfur atom in the  $\text{HSO}_3^-$  ion (bisulfite) has an oxidation state of +4 and is a mild reducing agent (becoming  $\text{S}^{6+}$  in the sulfate ion). The iodine atom in the  $\text{IO}_3^-$  ion (iodate) has an oxidation state of +5 and is an oxidizing agent (decreasing in oxidation state to zero in  $\text{I}_2$ ).



Sodium bisulfite,  $\text{NaHSO}_3$ , is used as a cheap source of bisulfite ion. The mixture of products is evaporated to dryness, and the iodine is separated from the residue by sublimation.

The element iodine is used as an antiseptic<sup>1</sup>, in the preparation of other medicines, in dye compounds, and to make silver iodide for photographic film.

## THE HALIDES

The binary compounds of the halogens are called halides. Examples are calcium bromide,  $\text{CaBr}_2$ , carbon tetrachloride,  $\text{CCl}_4$ , iron(III) fluoride,  $\text{FeF}_3$ , and iodine bromide,  $\text{IBr}$ .

### METAL HALIDES

The elemental halogens are such active electron acceptors that they react with all metals, even the noble metals. The compounds formed with metals of the lowest electronegativity are definitely ionic. Such compounds are made up of any metal in groups IA and IIA and a halogen. Metals of intermediate electronegativity, which do not give up electrons so easily, form halides that are not completely ionic but somewhat covalent. The smaller and more positive the metal ion, the greater its attraction for electrons, and the more covalent will be the bond.

In Table 21-3 are listed a number of metal halides.<sup>2</sup> The metal halides exhibit properties that are common to all ionic and ionic-covalent compounds. Note the difference in the melting point of compounds that are mainly ionic as compared with substances that are ionic-covalent. Ionic substances tend to have high melting points, and covalent ones low (although there are many exceptions, such as the covalent  $\text{SiO}_2$  and  $\text{SiC}$ , which have extremely high melting points).

The water solubility of a substance is one of its important properties. As a class, the metal chlorides, bromides, and iodides are soluble. Exceptions are the silver, lead, and mercury(I) compounds, as shown in Table 4 in the Appendix. Fluorides tend to be less soluble than the other halides. It might be expected that the covalent-ionic halides would be only slightly soluble in water. This is not the case generally, because the covalent-ionic compounds often react with water (*hydrolyze*) instead of just dissolving.

The covalent character of some metal halides is revealed by the fact that they are soluble in relatively nonpolar liquids. Examples

<sup>1</sup> Tincture of iodine is an antiseptic. "Tincture" refers to a solution in which ethyl alcohol is the solvent.

<sup>2</sup> As you study the metal halides, it will be well to keep in mind that there are some compounds of the so-called *halogenoid ions* which have properties similar to those of halide compounds. Examples of these ions are the cyanide,  $\text{CN}^-$ , and the thiocyanate,  $\text{SCN}^-$ , ions. By analogy with the compounds listed in Table 21-3, we would expect sodium cyanide,  $\text{NaCN}$ , to be ionic and soluble in water, and silver cyanide,  $\text{AgCN}$ , to be ionic-covalent and insoluble in water.



## GROUP VIIA:

## THE HALOGEN FAMILY

include  $\text{AlCl}_3$  in carbon tetrachloride,  $\text{FeCl}_3$  in ether, and  $\text{SnI}_4$  in carbon disulfide. The ionic halides are practically insoluble in such liquids.

TABLE 21-3 *Properties of metal halides*

name	formula	appearance	bond type*	melting point, °C	$\Delta H_f$ per equiv. wt, kcal†
tin(IV) chloride	$\text{SnCl}_4$	colorless liquid	c-i	-33	-31
aluminum chloride	$\text{AlCl}_3$	white powder	c-i	183	-55.6
iron(III) chloride	$\text{FeCl}_3$	dark brown crystals	c-i	282	-32.1
tin(IV) iodide	$\text{SnI}_4$	yellow crystals	c-i	340	?
silver chloride	$\text{AgCl}$	white powder	i-c	455	-30.4
silver fluoride	$\text{AgF}$	yellow powder	i-c	435	-48.7
lithium iodide	$\text{LiI}$	white crystals	?	446	-64.8
tin(IV) fluoride	$\text{SnF}_4$	white powder	i	705 (subl.)	?
potassium iodide	$\text{KI}$	colorless crystals	i	723	-78.3
sodium chloride	$\text{NaCl}$	colorless crystals	i	804	-98.2
aluminum fluoride	$\text{AlF}_3$	colorless crystals	i	900	-110
sodium fluoride	$\text{NaF}$	colorless crystals	i	990	-136.0
magnesium fluoride	$\text{MgF}_2$	colorless or violet crystals	i	1396	-131.9

\*Very largely ionic, i; more ionic than covalent, i-c; more covalent than ionic, c-i.

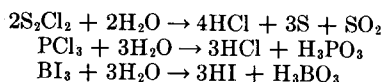
†In the formation of one equivalent of each of these substances, the same number of halogen atoms will be involved:  $6.02 \times 10^{23}$  atoms.

## NONMETAL AND METALLOID HALIDES

The compounds formed by the halogens with other nonmetals and with the borderline elements (metalloids) are covalent. Fluorine reacts directly with all the nonmetals except nitrogen, oxygen, and the lighter noble gases; chlorine reacts directly with all the nonmetals except nitrogen, oxygen, carbon, and the noble gases. Compounds of these elements (except for some noble gases) can be formed by indirect methods. Among the more interesting nonmetal halogen compounds are boron trifluoride,  $\text{BF}_3$ , silicon tetrafluoride,  $\text{SiF}_4$ , carbon tetrachloride,  $\text{CCl}_4$ , phosphorus trichloride,  $\text{PCl}_3$ , phosphorus pentachloride,  $\text{PCl}_5$ , antimony trichloride,  $\text{SbCl}_3$ , sulfur monochloride,  $\text{S}_2\text{Cl}_2$ , nitrogen trichloride,  $\text{NCl}_3$  (explosive), oxygen fluoride,  $\text{OF}_2$  (explosive), chlorine monoxide,  $\text{Cl}_2\text{O}$  (explosive), and the hydrogen halides,  $\text{HF}$ ,  $\text{HCl}$ ,  $\text{HBr}$ , and  $\text{HI}$ .

One of the fascinating developments of recent years has been the discovery of the reactivity of xenon, radon, and krypton with fluorine. The formulas and properties of some of the new fluorides formed by the noble gases are described in Chap. 29.

Many nonmetal and metalloid halides are extremely reactive and must be kept out of contact with water or even moist air. They may undergo hydrolysis readily, yielding acidic solutions. Examples of such reactions include



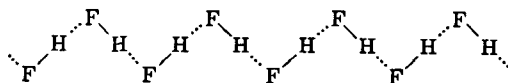
**Hydrogen Halides.** The hydrogen halides are so important to the study and practice of chemistry that they are given special attention. Their properties, summarized in Table 21-4, have two important characteristics: (1) the trends from chloride to bromide to iodide are as predicted from their location in the periodic table; and (2) the fluoride compound does not conform to the boiling and melting point trends, probably because of the small size and high electronegativity of the fluorine atom.

*Properties of hydrogen halides*

TABLE 21-4

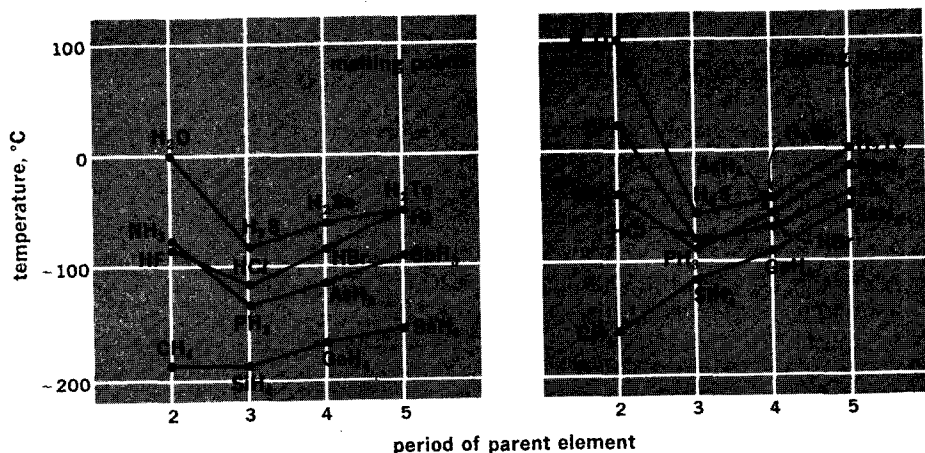
	HF	HCl	HBr	HI
boiling point, °C	20	-85	-67	-36
melting point, °C	-83	-114	-87	-51
% dissociation at 1000°	too slight to measure	0.0014	0.50	33
solubility at 20° and 1 atm, g/100 g H <sub>2</sub> O	35.3	42	49	57
$\Delta H^\circ$ per mole for $\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{X}_2 \rightarrow \text{HX}$ , kcal	-64	-22	-8.7	+6.2
color	none	none	none	none
odor	all very irritating; attack delicate nasal tissues			

For covalent compounds that are of the same general nature it is usual for the boiling and melting points to decrease as the molecular weights decrease. But hydrogen fluoride does not show this behavior, because the HF molecules are so strongly attracted to one another (via hydrogen bonds) that they form zigzag chains that act like larger molecules:



Therefore, the boiling and melting points of HF are abnormally high, as shown in Table 21-4. This behavior is shown graphically in Fig. 21-7, where it is related to similar effects for H<sub>2</sub>O and NH<sub>3</sub>.

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THE HALOGEN FAMILY**



**FIG. 21-7** The melting and boiling points of the hydrogen compounds of Groups IVA, VA, VIA, and VIIA. (Redrawn by permission from L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, 1940.)

Strong hydrogen bonds are formed only by small atoms, such as fluorine, oxygen, and nitrogen. It appears that a free pair of electrons in a small atom is more available to the hydrogen of another molecule than is a free pair in a large atom. In the larger orbitals of atoms, such as chlorine, sulfur, or phosphorus, the two electrons are probably not sufficiently localized to attract a hydrogen atom. Noting positions for CH<sub>4</sub> in Fig. 21-7, we realize that the carbon, though a small atom, has no free electron pair and can form no hydrogen bonds. The low melting and boiling points of methane indicate that CH<sub>4</sub> molecules are attracted to one another only by van der Waals forces.

Each of the HX compounds can be prepared by a reaction between hydrogen and the corresponding elemental halogen,  $H_2 + X_2 \rightarrow 2HX$ . This reaction, explosively exothermic in the case of F<sub>2</sub>, decreases in violence from fluorine to iodine, as can be seen by comparing the heat evolved per mole of HX formed (Table 21-4).

The stability of the compounds can be correlated with the energy of formation. The greater the energy of formation, the more stable the compound—HF is more stable than HI. The percentage dissociation at 1000° is a quantitative measure of the strength of the various H—X bonds; the H—I bond is weakest of the four.

All the hydrogen halides are shown to be covalent compounds by the fact that the pure liquid substances do not conduct an electric current. However, when dissolved in water, HCl, HBr, and HI form strong acid solutions; HF forms a weak acid solution, because the strong HF bond prevents a complete reaction with the H<sub>2</sub>O molecules to form H<sub>3</sub>O<sup>+</sup> and F<sup>-</sup>. The water solutions of all these com-

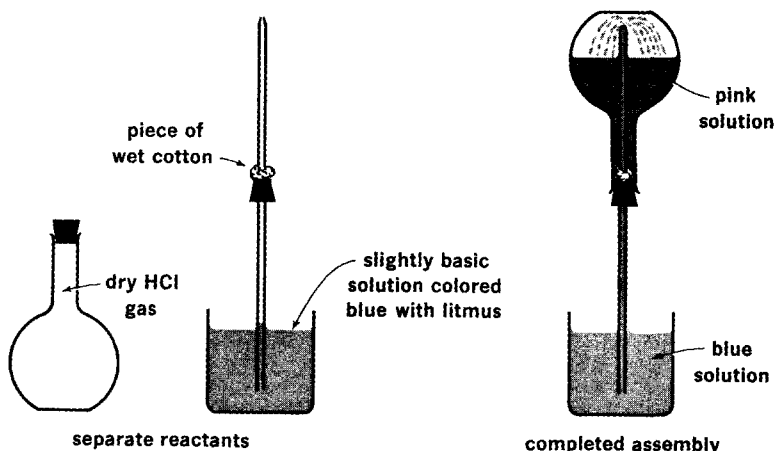
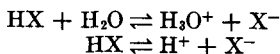


FIG. 21-8

The hydrogen chloride "fountain." To make the fountain operate, the stopper is removed from the flask of dry gas and the flask is then quickly inverted and set tightly on the rubber stopper on which there is some wet cotton. The water in the cotton dissolves the hydrogen chloride gas so completely that the pressure inside the flask decreases sharply. Atmospheric pressure forces the water in the beaker up the tube and into the flask. If the solution in the beaker is slightly basic, a little litmus indicator will color it blue, and the hydrochloric acid solution that is formed in the flask will turn the litmus pink.

pounds are called *hydro- -ic* acids; they conduct an electric current because of the presence of hydronium ions and halide ions:



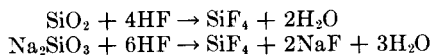
All the hydrogen halides form constant-boiling mixtures with water (see Chap. 10). The solubilities are quite striking when the volume of gas is considered (Fig. 21-8). At 20°C and 1.0 atm, 264 liters of gaseous hydrogen chloride will dissolve in 1 liter of water. Still there are almost five H<sub>2</sub>O molecules for every HCl molecule that has dissolved.

Hydrochloric acid, often called muriatic acid commercially, is by far the most important of the four acids. It is used to remove rust from scrap iron, to clean mortar from masonry, to prepare metal surfaces for electroplating, and to neutralize basic solutions. Hydrobromic and hydriodic acids are not widely used, because, although chemically almost identical to hydrochloric, they are much more expensive. Their solutions act as typical sources of hydrogen ions in neutralizing bases and dissolving active metals and oxides.

Hydrofluoric acid, unlike the other three, attacks glass and hence is used to etch and frost glass. Very precise markings such as thermometer graduations and even pictures can be etched out of the glass

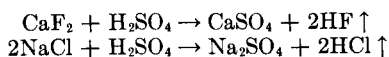
**GROUP VIIA:**  
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surface. The glass is first completely covered with a thin film of melted paraffin; the wax is then carefully cut away so as to expose the parts that are to be etched. Fumes of HF do not attack the paraffin but they do attack the silicon-containing compounds in the glass. The chemical reaction destroys the glass as the result of the formation of the gaseous silicon compound, SiF<sub>4</sub>. The reactions with silicon dioxide and sodium silicate, two compounds that react in a way similar to glass, are as follows:



Concentrated solutions of HCl, HBr, and HI can be shipped in steel or glass containers, but HF solutions must be kept in wax-lined vessels or special plastic tanks.

**PRODUCTION OF HYDROFLUORIC AND HYDROCHLORIC ACIDS.** Hydrogen fluoride and hydrogen chloride are usually prepared commercially by the action of hot concentrated H<sub>2</sub>SO<sub>4</sub> on a halide, for example, CaF<sub>2</sub> and NaCl:



This important type of reaction is mentioned again on page 599. Hydrogen bromide and hydrogen iodide cannot be prepared in this way, because Br<sup>-</sup> and I<sup>-</sup> ions are oxidized by hot concentrated H<sub>2</sub>SO<sub>4</sub> to the respective elements.

A more modern process of making hydrogen chloride involves a direct combination of hydrogen and chlorine. Both of these gases are produced during the electrolysis of aqueous sodium chloride; and in regions where electric power is cheap, it is economical to produce these gases for the purpose of making hydrogen chloride. The explosive photochemical chain reaction between hydrogen and chlorine can be controlled by means of an apparatus such as that in Fig. 21-9.

The chlorine and hydrogen gases are mixed in a burner in the same way that methane and air or acetylene and oxygen are mixed in laboratory burners. The hydrogen can be said to be burning in an atmosphere of chlorine. Only a slight excess of hydrogen is present, so that the gas produced runs as high as 99.0 per cent HCl.

Cool water is circulated through a water jacket around the burner to keep the temperature of the reacting gases below the point at which the reaction becomes explosive. The gaseous HCl goes out the top of the burner and down through pipes made of fused silica or tantalum in which flowing water absorbs the HCl to form hot concentrated acid. The hot acid is so corrosive that few materials can resist its attack completely. Total production of HCl in the United States is now about 1 million tons annually.

Hydrogen chloride burner for the combination of hydrogen and chlorine gas. (Photograph courtesy of Hooker Chemical Corporation.)

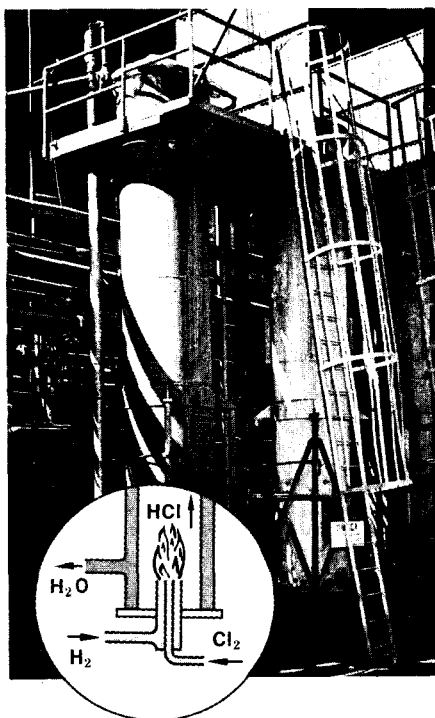


FIG. 21-9

## OXY-ACIDS AND OXY-SALTS

Compounds containing the ions  $\text{ClO}_4^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_2^-$ , and  $\text{ClO}^-$  are well known. In these compounds the oxidation state of chlorine is +7, +5, +3, and +1, respectively (see Fig. 5-1). Bromine and iodine form some similar oxy-ions, as shown in Table 21-5, but fluorine, which shows only the -1 state in any of its compounds, does not. The hydrogen compounds  $\text{HXO}_4$ ,  $\text{HXO}_3$ ,  $\text{HXO}_2$ , and  $\text{HXO}$  are acids and oxidizing agents. The salts of these acids, especially the sodium and potassium salts, also frequently serve as oxidizing agents.

### Group VIIA oxy-acids and oxy-ions

TABLE 21-5

oxidation state	name of acid	examples	name of anion
+1	hypo- -ous	$\text{HClO}$ , $\text{HBrO}$ , $\text{HIO}$	hypo- -ite
+3	-ous	$\text{HClO}_2$	-ite
+5	-ic	$\text{HClO}_3$ , $\text{HBrO}_3$ , $\text{HIO}_3$	-ate
+7	per- -ic	$\text{HClO}_4$ , $\text{HIO}_4$	per- -ate

**GROUP VIIA:  
THE HALOGEN FAMILY**

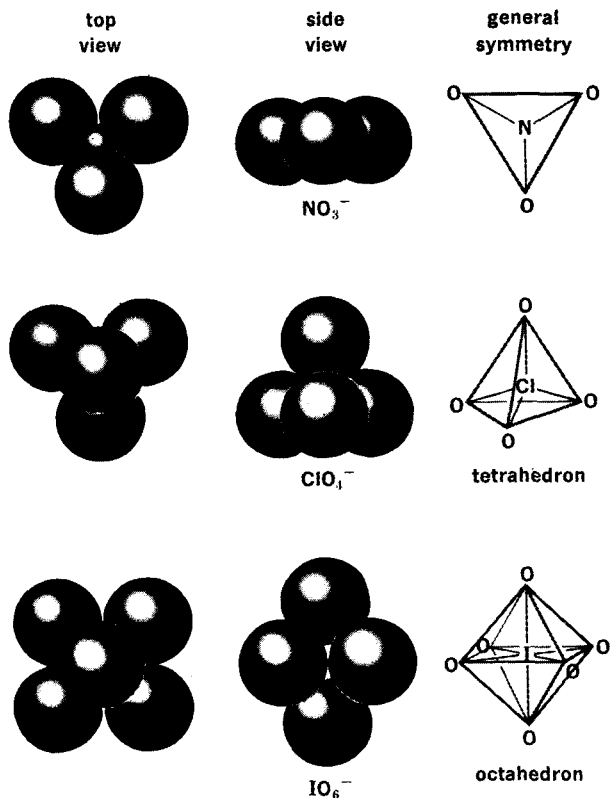


FIG. 21-10

Representatives of three common oxy-ion structures.

### NAMING OF OXY-IONS AND THEIR COMPOUNDS

A number of elements other than the halogens form oxy-acids. Structural models of three representative oxy-ions are shown in Fig. 21-10. Because of the great number and importance of oxy-ions, a system of naming them has been worked out. According to this system, the names of the oxy-acids and oxy-salts in a given family of elements include appropriate suffixes (and prefixes, if needed) to indicate the oxidation state of the parent element. The system, which is illustrated in Table 21-5 for the halogen compounds, is as follows:

1. Some common acid in the family is arbitrarily called the *-ic* acid. (In the case of the halogens,  $\text{HClO}_3$  is designated as chloric acid.) The name of a salt of this acid ends in *-ate*.

2. An acid whose parent atom has an oxidation state next lower than the *-ic* acid (one less oxygen atom) is called the *-ous* acid. The name of a salt of this acid ends in *-ite*.

3. When more than two oxygen acids of an element exist, the acid in which the oxidation state of the parent atom is higher than it is in the -ic acid (one more oxygen atom) is called the *per-* -ic acid. A salt of this acid is a *per-* -ate salt.

4. An acid in which the oxidation state of the parent atom is lower than it is in the -ous acid is called the *hypo-* -ous acid. A salt of this acid is a *hypo-* -ite salt.

5. The root of the name of the acid or the salt indicates the parent atom.

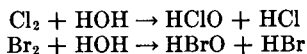
The following examples will help clarify the nomenclature: hypoiodous acid is HIO; perchloric acid is HClO<sub>4</sub>; sodium iodate is NaIO<sub>3</sub>; and calcium hypochlorite is Ca(ClO)<sub>2</sub>. Although oxy-compounds of nonhalogen elements will be taken up in other chapters, a few examples of naming are: nitric acid is HNO<sub>3</sub>; potassium nitrite is KNO<sub>2</sub>; sulfurous acid is H<sub>2</sub>SO<sub>3</sub>; and magnesium sulfate is MgSO<sub>4</sub>.

Note in Table 21-5 that the central atom changes in oxidation state by two units each time it gains or loses one oxygen atom. When an element forms a number of oxy-acids, the most stable one usually has a structure in which the central atom is surrounded by as many oxygen atoms as can fit around it. Also, the strengths of acids in such a series increases as the number of coordinated oxygen atoms increases. The following three series bear out these statements:

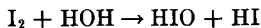
	HClO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub>	HNO <sub>3</sub>	
less	HClO <sub>3</sub>	H <sub>2</sub> SO <sub>3</sub>	HNO <sub>2</sub>	acid
stable	HClO <sub>2</sub>			strength
	HClO			

## PREPARATION OF OXY-HALOGEN COMPOUNDS

Dilute solutions of hypochlorous and hypobromous acids are readily prepared by the action of chlorine and bromine with water:

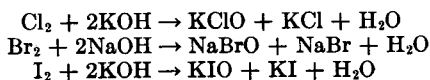


Iodine reacts very slowly to form hypoiodous acid:



These HXO compounds are too unstable to be obtained in the pure form. They are prepared and used only in dilute solutions.

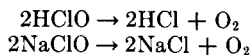
As we would expect from the foregoing equations, the action of a halogen with a water solution of a base results in the formation of two salts (one of the hypohalogen acid and one of the hydrohalogen acid):



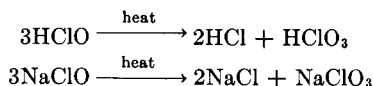


**GROUP VIIA:**  
**THE HALOGEN FAMILY**

The hypohalogen salts,  $\text{MXO}$ , are considerably more stable than the hypohalogen acids,  $\text{HXO}$ , but both tend to decompose on standing:



When heated, dilute solutions of the oxy-ions undergo a type of internal oxidation-reduction (this is discussed below under potassium chlorate). For hypochlorous acid and sodium hypochlorite the reactions are



### IMPORTANT SALTS

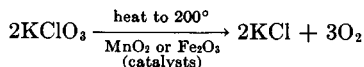
The salts of the halogen oxy-ions include a number of common, useful substances. Chemically speaking, these salts can be thought of as sources of the various oxy-ions. Because of the relative costs, the chlorine compounds are much more widely used than the bromine and iodine compounds.

*Sodium hypochlorite*,  $\text{NaClO}$ , is the source of the active ion in Clorox, a household disinfectant and bleach. It is formed by passing chlorine into dilute sodium hydroxide.



No effort is made to separate the  $\text{NaCl}$  from the reaction product. Instead, the product is bottled and marketed as a mixture.  $\text{NaClO}$  and  $\text{NaCl}$  each constitutes about 5 per cent of the mixture, the remainder being water.

*Potassium chlorate*,  $\text{KClO}_3$ , is a compound that serves as a convenient laboratory source for oxygen gas because it is so easily decomposed:

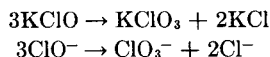


An interesting application of this characteristic is the inclusion of potassium chlorate with the combustible material in the head of a match (see Fig. 23-5). The initial combustion of the match does not depend on atmospheric oxygen; instead, the oxygen comes from the potassium chlorate. This compound is extremely dangerous when mixed with such combustible materials as paper, cloth, and sulfur. Under certain conditions combustion may begin without warning and proceed rapidly enough so that an explosion results.

Red flares (which can be explosive) sometimes contain a mixture of potassium chlorate, sugar, and strontium nitrate. The potassium chlorate acts as the oxidizer for the combustion of the sugar. The heat

from the reaction causes the strontium compound to emit red light. (Review flame spectra in Chap. 3.)

Potassium chlorate is formed by heating a solution of potassium hypochlorite:

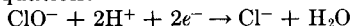


or

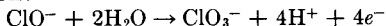


This reaction involves internal oxidation-reduction in which some of the chlorine atoms gain electrons and others lose. In the reduction equation, the chlorine oxidation state changes from +1 to -1; in the oxidation equation, from +1 to +5:

Reduction equation:



Oxidation equation:



*Potassium perchlorate*,  $\text{KClO}_4$ , is a more stable compound than potassium chlorate. Unlike the latter, it does not decompose unless heated to a high temperature. Flares, rocket propellant mixtures, fuse mixtures, and fireworks can be made from a very combustible material and powdered potassium perchlorate. Powdered active metals, such as aluminum and magnesium, burn fiercely when mixed with  $\text{KClO}_4$  and ignited.

From the formulas  $\text{KClO}_3$  and  $\text{KClO}_4$ , we might think that the perchlorate would liberate oxygen more readily than the chlorate, but this is not the case. Evidently the bonds in the tetrahedral  $\text{ClO}_4^-$  make possible a more tightly bonded packing, whereas those in the pyramidal  $\text{ClO}_3^-$  are strained and easily broken by a little energy of activation. Potassium chlorate is much more dangerous than potassium perchlorate for use in flares and pyrotechnics.

## CHAPTER REVIEW

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### Topics

Physical and chemical properties of the halogens, occurrence, preparation and uses of the halogens, halides in general, hydrogen halides, oxy-ions, oxidation-reduction reactions of halogens and their oxy-compounds.

### Exercises

1. Explain, on the basis of atomic theory, why the elements within a group at the left or right of the periodic table should be more similar to each other chemically than elements in a group toward the middle of the table.

**GROUP VIIA:**  
**THE HALOGEN FAMILY**

2. Today, atomic structure serves as a guide for organizing elements into families. What guides enabled fluorine, chlorine, bromine, and iodine to be recognized as a family before the theory of atomic structure had been developed?
3. Write a hypothetical nuclear equation for a bombardment reaction that would yield astatine.
4. Amounts of nuclides prepared by bombardment reactions are usually so small that special methods must be used to collect them for study. One way to remove a trace of  $\text{At}^-$  ion from a solution would be to precipitate a large amount of some compound with which the  $\text{At}^-$  ion might coprecipitate. Choose such a compound, tell how you would cause it to precipitate, and indicate why  $\text{At}^-$  might precipitate with it and why it might not.
5. Bromine, cesium, and gallium are liquid at or near room temperature. Consider various uses for mercury and discuss the possible substitution of each of these elements for mercury in each use.
6. Compare the statements, "The outer electrons in a fluorine atom are close to its nucleus; therefore its ionization energy is high" and "The ionization energy of fluorine is high; therefore we think the outer electrons of a fluorine atom are attracted strongly by the nucleus." Is there any important difference in these statements? Justify your answer carefully. Which statement do you prefer?
7. Show by consideration of specific enthalpy changes, which should yield more energy in reacting with hydrogen, liquid bromine or gaseous bromine at  $25^\circ$ .
8.
  - a. By means of diagrams show how the shielding effect differs for chlorine versus bromine.
  - b. Can the relative shielding effects of chlorine and bromine be correlated with their ionization energies and their electron affinities?
9.
  - a. The text states that  $\text{BrF}$  is polar. What sort of experimental evidence probably supports this statement?
  - b. One of the interhalogen compounds mentioned is  $\text{ClF}_3$ . If this substance were nonpolar, it would indicate the molecule had what shape? What shape(s) would be probable if the molecule were polar?
10. The hybridization for  $\text{IF}_5$  is thought to involve three  $6p$  and two  $6d$  orbitals. Work out an  $sp^3d^2$  hybridization diagram for the compound, similar to those in Table 19-9; the  $6s$  electrons can be thought of as the source of the lone pair.
11. Complete each of the following equations for which a reaction tends to occur:
  - a.  $\text{Mg} + \text{Br}_2 \rightarrow$
  - b.  $\text{Cl}_2 + \text{I}_2 \rightarrow$
  - c.  $\text{F}_2 + \text{H}_2\text{O} \rightarrow$
  - d.  $\text{Cl}_2 + \text{NaF} \rightarrow$
  - e.  $\text{Ag} + \text{Br}_2 \rightarrow$
  - f.  $\text{I}_2 + \text{Pt} \rightarrow$
12.
  - a. Consider the structure given in Fig. 21-2 for  $\text{ClF}_4^-$ . What general rule would indicate that the nonbonding electron pairs should be at opposite corners of the octahedron?

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**GROUP VIIA:**  
**THE HALOGEN FAMILY**

23. In the commercial production of bromine, explain why  $\text{Br}^-$  is changed to  $\text{Br}_2$ , then back to  $\text{Br}^-$  again, before being changed finally to  $\text{Br}_2$ .
24. Which do you think might be more ionic,  $\text{FeCl}_2$  or  $\text{FeCl}_3$ ;  $\text{AlI}_3$  or  $\text{AlF}_3$ ;  $\text{AlCl}_3$  or  $\text{KCl}$ ;  $\text{NaCl}$  or  $\text{SnCl}_4$ ? Justify your choice in each case.
25. Starting with potassium iodide,  $\text{KI}$ , outline, with equations where possible, a method of producing iodine in the laboratory and purifying it.
26.
  - a. In general, for metal halides, how are enthalpies of formation related to bond types, covalent versus ionic?
  - b. In general, for metal halides, how are enthalpies of formation related to melting points? Is there another enthalpy quantity that might be related to melting points in roughly the same way?
27.
  - a. Write equations for the hydrolysis of phosphorus triiodide and boron tribromide.
  - b. In the presence of sulfuric acid,  $\text{H}_2\text{SO}_4$ , would the hydrolyses just written tend to occur to the same extent as in plain water?
28. The  $\Delta H_{\text{vap}}$  in kilocalories per mole at the boiling point for the hydrogen halides are as follows:  $\text{HF}$ , 7.24;  $\text{HCl}$ , 3.85;  $\text{HBr}$ , 4.21; and  $\text{HI}$ , 4.72. How well is Trouton's rule obeyed by these compounds? Discuss any discrepancies. (See Exercise 47, Chap. 16.)
29. Write equations for two general methods of preparing hydrogen halides.
30. Hydrochloric acid is used to remove rust,  $\text{Fe}_2\text{O}_3$ , from iron prior to plating the iron with zinc or other protective metals. Write an equation that accounts for the cleaning process. Why is hydrobromic acid not used for this purpose?
31. By means of an equation, show why it is dangerous to have a cyanide, say  $\text{NaCN}$ , dissolved in acid solution, especially if the solution is concentrated or hot.
32.
  - a. Fluorine or chlorine could be used as oxidizing agents for hydrogen in a rocket engine. Using the data in Table 21-4, calculate the heat evolved when 1 ton of hydrogen reacts with chlorine, and then do a similar calculation for fluorine.
  - b. If the reactants just described are held as liquids in the rocket, will the heat evolved in the overall reaction to yield hot gases be greater or less than if they are held as gases?
33. At one time it was common to refer to gases formed in chemical reactions as *nascent* (new-born). During the process of formation active species are apparently formed that are more reactive than ordinary samples of gas; for example, nascent hydrogen is more active than ordinary  $\text{H}_2$ . Cite two examples that show that in the forming of gases at electrodes, the elements are very active as formed.
34. Write balanced equations for the preparation of the following:
  - a. Bromine pentafluoride
  - b. Copper(I) iodide
  - c. Calcium hypochlorite
  - d. Fluorine from calcium fluoride
  - e. Carbon tetrachloride from methane,  $\text{CH}_4$
  - f. Gold(III) bromide
  - g. Arsenic trichloride
  - h. Potassium chlorate

35. Write a balanced equation for the (violent) reaction between aluminium and potassium perchlorate.
36. Write a balanced equation for the reaction of iodine and chlorine in water solution to give iodic acid and hydrochloric acid.
37. a. Name the following:  
 $\text{LiIO}$ ,  $\text{HBrO}_3$ ,  $\text{CsClO}_4$ ,  $\text{Ca}(\text{ClO})_2$ .  
 b. Write formulas for the following: barium periodate, sodium chlorate, magnesium hypochlorite, chlorous acid.
38. "Hydrofluoric acid is a weak acid; therefore it does not attack containers so readily as a strong acid, such as hydrochloric acid." Discuss this statement.
39. In Fig. 21-7 the anomalous positions of  $\text{HF}$ ,  $\text{H}_2\text{O}$ , and  $\text{NH}_3$  are attributed to hydrogen bonding. What seems to be the explanation for the decreased importance in this type of bonding in  $\text{HCl}$ ,  $\text{H}_2\text{S}$ , and  $\text{PH}_3$ ; in  $\text{CH}_4$ ?
40. Cite two factors that help account for the regular change in the boiling points of similar substances, such as  $\text{He}$ ,  $\text{Ne}$ , and  $\text{Ar}$  or  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_8$ .
41. Calculate the molalities and mole fractions of solute for the saturated hydrogen halide solutions described in Table 21-4.
42. From the percentage of dissociation of  $\text{HI}$  at  $1000^\circ$ , calculate  $K_p$  and  $\Delta G_f^\circ$  for the formation of  $\text{HI}$  at that temperature.
43. The value of the heat of formation of  $\text{HI}$  in Table 21-4 is based on  $\text{I}_2(s)$  as a reactant. For comparison, calculate  $\Delta H_f^\circ$  at  $25^\circ$  based on  $\text{I}_2(g)$  as a reactant. See Table 16-6 for data.

## SUPPLEMENTARY READING

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**GROUP VIA:****THE SULFUR FAMILY**

Moving from the halogens to the vertical column of elements to the left of them in the periodic table brings us to group VIA. In order of increasing atomic number, these elements are oxygen, sulfur, selenium, tellurium, and polonium.

Typical of a period 2 element, oxygen is so different in physical and chemical properties from the other members of the group that it is conveniently studied separately. Also, it is so important early in the study of chemistry that it was treated in some detail in Chap. 6. In contrast, polonium is so rare that its chemistry is relatively unimportant. It is of some interest because of its radioactivity (see Fig. 14-6).

In the present discussion we shall consider sulfur, S, selenium, Se, and tellurium, Te, as a family, oxygen being mentioned from time to time for comparison. Each element in family VIA has six electrons ( $s^2p^4$ ) in its outside main energy level.

**PROPERTIES OF THE SULFUR FAMILY****PHYSICAL PROPERTIES**

Some of the physical properties of elements in the sulfur family are listed in Table 22-1. It can be seen at a glance that oxygen is quite unlike the other three. As far as trends are concerned, oxygen does not fit well into the series because it has too low a melting point, boiling point, and atomic radius; it has too high an ionization energy and an electronegativity. The important trends to note in Table 22-1 are (1) an increase in melting and boiling point and atomic radius as the atomic number increases, and (2) a decrease in ionization energy and

**GROUP VIA:  
THE SULFUR FAMILY**

electronegativity as the atomic number increases. The sizes of these atoms are shown to scale in Fig. 22-1.

Group VIA provides a good example to support the generalization that, as the atomic number increases in an A family, the elements become more metallic in character. Whereas oxygen and sulfur are typical nonmetals with low electrical and heat conductivities, tellurium approaches some metals in electrical conductivity. Also tellurium and one form of selenium look like metals. The metallic form of selenium has a rare property that is noteworthy—its electrical conductivity, though low, is greatly increased when light shines on it.

Relative sizes of the atoms in the VIA family.

Hence selenium is used in instruments designed for measuring the intensity of light (even that from stars) and in automatic switches that turn lights on when the sun sets and turn them off again at daybreak.

As noted in Table 22-1, selenium may be either red or gray. This suggests that this element exists in more than one crystalline form. Similar polymorphism is exhibited by sulfur, but both common crystalline forms are yellow in color. Actually more than 30 allotropes of sulfur are known, but most are unstable. In addition to existing in one or more crystalline modifications, sulfur, selenium, and tellurium

  
O 0.66 A

  
S 1.04

  
Se 1.14

  
Te 1.32

FIG. 22-1

*Physical properties of the sulfur family*

TABLE 22-1

	oxygen O	sulfur S	selenium Se	tellurium Te
appearance at room temperature	colorless gas	yellow brittle solid	red or gray solid	silver-white solid
molecular formula	O <sub>2</sub>	S <sub>2</sub> , S <sub>4</sub> , S <sub>6</sub> , S <sub>8</sub>	Se <sub>2</sub> , Se <sub>8</sub>	Te <sub>2</sub> , (Te <sub>8</sub> ?)
melting point, °C	-218.8	119.0	217	450
boiling point, °C	-183	444.6	685	1087
ionization energy, ev	13.55	10.36	9.75	9.01
	(312 kcal)	(239 kcal)	(225 kcal)	(208 kcal)
radius of atom, A	0.66	1.04	1.14	1.32
radius of ion (E <sup>2-</sup> ), A	1.40	1.84	1.98	2.21
electronic structure	2,6	2,8,6	2,8,18,6	2,8,18,18,6
electronegativity	3.5	2.5	2.4	2.1

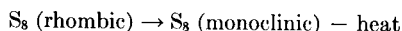
can be prepared in the plastic or *amorphous* condition by suddenly freezing the hot liquid elements. When solid sulfur is formed very rapidly (for example, by pouring the boiling liquid into cold water), the sulfur molecules do not have time to orient themselves so as to form a well-developed crystal. As a result, the solid is a mass of tiny crystallites that have no overall pattern; that is, they are amorphous.

It is not uncommon for pure substances to exist in more than one crystal pattern, depending on the temperature and pressure, and in some cases on the method of preparation. Sulfur is a good example of a

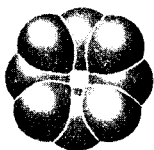


**GROUP VIA:  
THE SULFUR FAMILY**

substance that behaves in this manner. When a solution of sulfur in toluene is evaporated to dryness, the sulfur will crystallize in a rhombic lattice if the temperature is below 95.5°C, but it will crystallize in a monoclinic lattice if the temperature is above this. A **transition temperature** between crystal forms is usually just as definite a point as a boiling or freezing point. Furthermore, such a change in form involves a change in energy. In sulfur the change from rhombic to monoclinic is endothermic, because the molecules are not packed together so closely in the monoclinic pattern as in the rhombic:



When solid sulfur in the rhombic form is raised to a temperature above 95.5°C, the crystalline pattern slowly changes to monoclinic. The complete transformation may take days, because the molecules in the solid cannot move easily enough to reorient themselves quickly in the new crystal pattern.



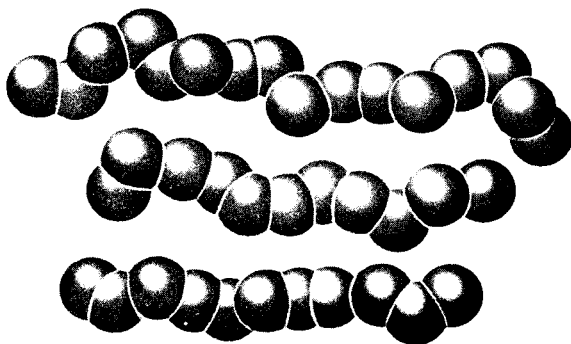
Top and side views of a model of the sulfur molecule,  $\text{S}_8$ .

The sulfur molecule, consisting of a ring of eight atoms, is pictured in Fig. 22-2. This is the unit particle commonly present in the solid and liquid states, although the rings tend to break up and form chains when the sulfur is heated.



FIG. 22-2

The existence of these chains explains the peculiar changes in the viscosity of liquid sulfur. Instead of decreasing regularly between melting and boiling temperatures, the viscosity of sulfur decreases from 119° to a minimum at about 160°, after which the viscosity begins to increase drastically, reaching a maximum at about 200°; above 200° the viscosity decreases till the boiling point of 444.6° is reached. When sulfur first melts, it can be poured easily from a beaker



Models representing the chains of sulfur atoms in viscous, molten sulfur.

FIG. 22-3

or test tube, but at about 200° it has the consistency of thick tar. Evidently the sulfur molecules still exist as  $\text{S}_8$  rings just above the melting point, and these rings slip and roll over one another easily (not

viscous). But when the liquid sulfur is heated, the rings are broken into chains that then join, forming very long molecules (see Fig. 22-3); these long molecules become entangled with one another (very viscous).<sup>1</sup> Above about 200° these chains break up more and more, and sulfur begins to act again like a typical liquid; that is, the viscosity begins to decrease with further rise in temperature.

## CHEMICAL PROPERTIES

A distinctive feature of the elements in the sulfur family is the fact that their atoms have four *p* electrons in the outside energy level. They therefore frequently react as oxidizing agents, achieving an oxidation state of -2. From the relative sizes of the atoms (Fig. 22-1), it would be expected that oxygen would be the strongest oxidizing agent and tellurium the weakest. This is indeed the case, as shown by the electronegativity data in Table 22-1. Sulfur, selenium, and tellurium can be oxidized by strong oxidizing agents—for example, oxygen or some of the halogens. When oxidized, the elements tend to be in the +4 or +6 oxidation state, as in SO<sub>2</sub>, SeO<sub>2</sub>, TeO<sub>2</sub>, and SO<sub>3</sub>, SeO<sub>3</sub>, TeO<sub>3</sub>. However, other oxidation states are known.

The most common inorganic compounds of sulfur are the sulfides and sulfates, containing S<sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> ions, respectively. The sulfites contain SO<sub>3</sub><sup>2-</sup> and are well known, as are a number of other combining forms:

Oxidation state:	-2	0	+4	+6
Examples:	H <sub>2</sub> S	S	SO <sub>2</sub> H <sub>2</sub> SO <sub>3</sub>	SO <sub>3</sub> H <sub>2</sub> SO <sub>4</sub>
	H <sub>2</sub> Se	Se	SeO <sub>2</sub> H <sub>2</sub> SeO <sub>3</sub>	SeO <sub>3</sub> H <sub>2</sub> SeO <sub>4</sub>
	H <sub>2</sub> Te	Te	TeO <sub>2</sub> H <sub>2</sub> TeO <sub>3</sub>	TeO <sub>3</sub> H <sub>2</sub> TeO <sub>4</sub>

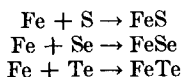
To metals sulfur acts as an electron acceptor; to most nonmetals as a donor. The fact that it is both an oxidizing and a reducing agent accounts for its combining with all the elements save gold, platinum, and the noble gases. Yet sulfur is not very reactive unless heated above its melting point.

Selenium and tellurium have similar chemical properties but are somewhat less reactive than sulfur. Selenium compounds are so poisonous that in some regions the small amount of selenium taken from the soil by growing plants is enough to poison livestock (blind staggers).

<sup>1</sup> This modern explanation is not unlike that given in the first century B.C. by the Roman poet Lucretius (as translated by R. E. Latham): "We see that wine flows through a strainer as fast as it is poured in; but sluggish oil loiters. This, no doubt, is either because oil consists of larger atoms, or because these are more hooked and intertangled and, therefore, cannot separate as rapidly, so as to trickle through the holes one by one."

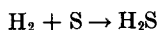
**GROUP VIA:  
THE SULFUR FAMILY**

**Reactions with Metals.** The equations below represent the type of reaction that occurs between a metal and members of the sulfur family:



As a rule, sulfur reacts more energetically than selenium and tellurium, and less energetically than oxygen. The heat evolved when a powdered metal is oxidized by powdered sulfur may be great enough to make the products red-hot. Some metals—among them copper, silver, and mercury—show a greater chemical affinity for sulfur than for oxygen. This is the opposite of what would be predicted on the basis of the electronegativities: O, 3.5; S, 2.5. The explanation is that a stronger crystal is formed when the larger sulfide ion is distorted or *polarized* by these small positive metal ions.

**Reactions with Hydrogen.** When hydrogen gas is bubbled through molten sulfur, the two elements react to form the gas hydrogen sulfide:



The compounds  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$  can also be prepared by direct combination of the elements.

**Reactions with Certain Nonmetals.** Sulfur reacts with hot carbon to form the colorless liquid carbon disulfide,  $\text{CS}_2$ , and with hot boron to form the solid boron trisulfide,  $\text{B}_2\text{S}_3$ . The bonds in these two compounds are covalent, the electron pair being relatively closer to the sulfur atom.

Sulfur burns in oxygen and in fluorine to form gaseous oxides,  $\text{SO}_2$  and  $\text{SO}_3$ , and a gaseous fluoride,  $\text{SF}_6$ , respectively. It reacts less violently with chlorine to form the liquid sulfur monochloride,  $\text{S}_2\text{Cl}_2$ . The bonds in all these compounds are covalent, but the electron pairs are drawn away from the sulfur atom so that sulfur is relatively positive.

Note that, when the sulfur atom is relatively negative (oxidation state of  $-2$ ), its symbol is placed second in the formula and the compound is called a *sulfide*; when the sulfur atom is relatively positive (oxidation state of  $+1$ ,  $+4$ , or  $+6$ ), its symbol is placed first and the compound is called an *oxide* or a *halide*, as the case may be.

## **OCCURRENCE**

About the same amount of sulfur as of fluorine is present in the earth's crust, approximately 0.1 per cent by weight. Selenium and tellurium are rare; the relative abundance of the two, taken together, is less than a millionth that of sulfur.

All three occur naturally, both in the free form and in compounds.

Although most sulfur is found combined with metals in compounds, such as those listed in Table 22-2, large deposits of elemental sulfur have been found. Elemental selenium is often found mixed with the

*Abundant sulfur-containing minerals*

**TABLE 22-2**

formula	chemical name	mineral name
S	sulfur	sulfurite
FeS <sub>2</sub>	iron(II) disulfide	pyrite
HgS	mercury(II) sulfide	cinnabar
PbS	lead sulfide	galena
ZnS	zinc sulfide	sphalerite
CuFeS <sub>2</sub>	copper(II) iron(II) sulfide	chalcopyrite
BaSO <sub>4</sub>	barium sulfate	barite
CaSO <sub>4</sub> ·2H <sub>2</sub> O	calcium sulfate dihydrate	gypsum

sulfur. When sulfur occurs as the element, it is usually mixed with rocks and earth; such a mixture is easily separated by heating it until the sulfur melts and runs out. The element was known to the ancients as *brimstone*, the stone that burns.

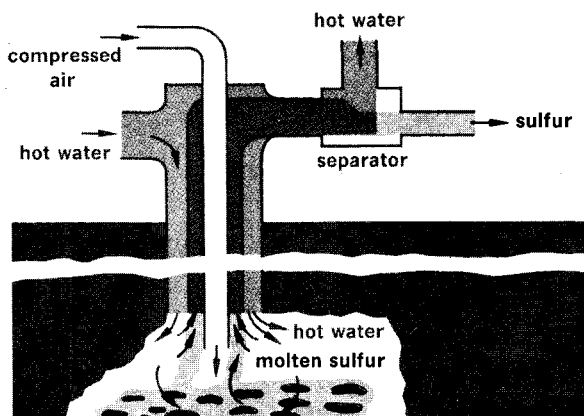
### PRODUCTION AND USES OF THE SULFUR FAMILY

Because sulfur is one of the most useful of all nature's raw materials, the United States is fortunate in having some of the world's richest deposits of elemental sulfur. Located on the Gulf Coast in Texas and Louisiana are huge beds of rock that are shot through with veins of sulfur. These sulfur-rock beds, roughly circular in shape and about half a mile across, are often found in the cap rock that covers great subterranean salt domes of sodium chloride. The fact that the sulfur is itself covered by several hundred feet of quicksand permeated by poisonous gases often makes shaft-mining impractical.

Till early in this century, most sulfur was obtained from volcanic sources; then an American engineer, Herman Frasch, devised the ingenious method now used for mining sulfur. A hole or well is drilled down into the sulfur-containing stratum, and three concentric pipes are lowered into it. The sulfur is melted in the rock bed by superheated water (the water is kept under sufficient pressure so that it can be heated to about 180°C). Compressed air forces the water-molten sulfur mixture up to the surface of the ground, where it is separated. (See Fig. 22-4.) The sulfur is then pumped into a storage vat where it cools and freezes (at 119°C), becoming part of a huge block of sulfur.

We can gain an idea of the immense scale of operations from the fact that such a block may be 400 ft long, 200 ft wide, and 100 ft high. When some of the sulfur is to be shipped, the required quantity is blasted off with dynamite; the broken sulfur is scooped up by a steam shovel and loaded onto freight cars on a railroad track laid right be-

**GROUP VIA:  
THE SULFUR FAMILY**



The Frasch process for mining sulfur.

FIG. 22-4

side the storage block, or onto conveyor belts to barges in the Gulf. Sulfur is even shipped in the molten form via ocean tankers.

In spite of the fact that little attention is given to purifying it or protecting it during storage and shipping, sulfur is one of the purest (99.5 per cent pure) of all the substances that are produced on a really large scale.

Elemental sulfur can be prepared by the oxidation of sulfides or the reduction of sulfites and sulfates. Selenium and tellurium can be prepared by similar reactions. In the case of sulfur, these reactions are not of primary industrial importance in this country, because the element itself can be mined so cheaply. Sulfur is also a by-product in the refining of certain sulfur-containing crude oils and in the treatment of some metal sulfides.

More than 7,400,000 tons of sulfur are produced annually in this country. A large portion of this is used in the manufacture of sulfuric acid,  $\text{H}_2\text{SO}_4$ . Considerable amounts are required for the vulcanization of rubber (Chap. 28), as a fuel in gunpowder and matches, for use in insecticides and soil conditioners, and for the manufacture of carbon disulfide (a solvent) and many other compounds.

Selenium is used in light-sensitive devices, for special vulcanizing processes for rubber, for ruby glass (red-colored glass), and in certain copper and steel alloys. An interesting, recently developed use is as the sensitive element in Xerox machines for photocopying.

Tellurium is used as an additive in some steel and lead alloys.

## **IMPORTANT COMPOUNDS OF THE SULFUR FAMILY**

### **HYDROGEN COMPOUNDS**

All five hydrogen compounds of the sulfur family are known: hydrogen oxide,  $\text{H}_2\text{O}$ , hydrogen sulfide,  $\text{H}_2\text{S}$ , hydrogen selenide,  $\text{H}_2\text{Se}$ , hydrogen telluride,  $\text{H}_2\text{Te}$ , and hydrogen polonide,  $\text{H}_2\text{Po}$ . Table 22-3 lists some of the important properties of the first four.

The trend in heat of formation is especially important, because it indicates the relative stability of the compounds.  $\text{H}_2\text{O}$  is by far the most stable,  $\text{H}_2\text{S}$  next, then  $\text{H}_2\text{Se}$ , and last,  $\text{H}_2\text{Te}$ . Hydrogen selenide and hydrogen telluride are actually endothermic compounds. Such

*Properties of hydrogen compounds of elements (E)  
of the sulfur family*

TABLE 22-3

	$\text{H}_2\text{O}$	$\text{H}_2\text{S}$	$\text{H}_2\text{Se}$	$\text{H}_2\text{Te}$
melting point, $^{\circ}\text{C}$	0	-85.6	-60.4	-51
boiling point, $^{\circ}\text{C}$	100	-60.8	-41.5	- 1.8
$\Delta H^{\circ}$ per mole for $\text{H}_2 + \text{E} \rightarrow \text{H}_2\text{E}$ , kcal	-68.3	- 4.8	+20.5	+36.9
first ionization constant, $\text{H}_2\text{E} \rightleftharpoons \text{H}^+ + \text{HE}^-$		$1.2 \times 10^{-7}$	$1.9 \times 10^{-4}$	$2.3 \times 10^{-3}$

compounds are usually unstable and will decompose with the evolution of energy if sufficient activation energy becomes available. This is the stability trend we would predict on the basis of the sizes of the atoms. The large tellurium atom has the least attraction for the electron pair joining it to the hydrogen atom, the selenium has more attraction, the sulfur atom still more, and the oxygen atom the most.

Note also the trend in the ionization constant,  $K_i$ , of the water solutions of these compounds:

$$K_i = \frac{[\text{H}^+][\text{HE}^-]}{[\text{H}_2\text{E}]}$$

The small value for  $\text{H}_2\text{S}$  indicates that this proton donor is holding on to its protons rather than letting them go to the  $\text{H}_2\text{O}$  molecules. The trend from  $\text{H}_2\text{S}$  to  $\text{H}_2\text{Te}$  reveals that the smaller sulfur atom holds on to hydrogen more tightly than the larger tellurium atom does. The water solutions of  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ , and  $\text{H}_2\text{Te}$  are acidic; hydro-telluric acid is the strongest of the three.

*Hydrogen sulfide* is an important chemical compound from the standpoint of general laboratory utility. It can be readily prepared by the action of acids on metallic sulfides. It is a poisonous gas whose offensive smell (rotten eggs) is well remembered by all who encounter it in the laboratory. Hydrogen sulfide is present in minute amounts in the fumes given off during the burning of sulfur-containing fuel oil and coal. It corrodes metals; for example, in air containing traces of  $\text{H}_2\text{S}$  silverware tarnishes, owing to the formation of a thin film of silver sulfide. The dark silver sulfide remains on the surface until buffed off.

Hydrogen sulfide dissolves in water and makes a slightly acidic solution, hydrosulfuric acid, which is widely used in qualitative analysis.

The salts of hydrosulfuric acid are the *sulfides* and the *acid sulfides*. Examples are sodium sulfide,  $\text{Na}_2\text{S}$ , sodium acid sulfide,  $\text{NaHS}$ , calcium sulfide,  $\text{CaS}$ , and calcium acid sulfide,  $\text{Ca}(\text{HS})_2$ . Solutions of the

**GROUP VIA:  
THE SULFUR FAMILY**

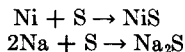
soluble sulfides are used to de-hair hides in the tanning industry. Some sulfide cosmetic preparations available in the stores have the same aim.

**SULFIDES, SELENIDES, AND TELLURIDES**

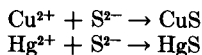
The metallic sulfides are important well-known compounds, because they occur widely as minerals and are often encountered in laboratory and industrial chemistry. The selenides and tellurides have similar formulas and structures but are relatively rare.

Except for the metals of very low electronegativity (metals in groups IA and IIA), the sulfides tend to be drawn by ionic-covalent bonds into tight structures that have rather high melting points and are very insoluble in water.

The metal sulfides are formed (1) by direct union of the finely ground elements or (2) by reaction between the ions in water solution. Direct union occurs in the following reactions:



Ionic reactions in solution include

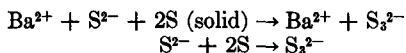


Aside from the metals in groups IA and IIA, the other metallic sulfides are characterized by their extremely slight solubility. From the solubility product of mercuric sulfide,  $K_{sp} = 3.5 \times 10^{-52}$ , it can be calculated that only one pair of ions ( $\text{Hg}^{2+}$ ,  $\text{S}^{2-}$ ) of mercuric sulfide is dissolved in 90 liters of the saturated solution. For many years the analytical chemist has taken advantage of the fact that the sulfides of many metals are so slightly soluble.

Nonmetallic sulfides are also well known, though as a rule they hydrolyze in contact with moist air. An exception to this rule is carbon disulfide,  $\text{CS}_2$ , a colorless liquid that neither reacts with nor mixes with water. Produced in the United States to the extent of about 700 million lb annually, carbon disulfide is used chiefly in the manufacture of rayon and cellophane (see Chap. 28) and of carbon tetrachloride. (See also Table 24-4.)

**METAL POLYSULFIDES**

Not only do sulfur atoms tend to bond together in elemental sulfur (as rings and chains), but they may attach themselves to the sulfide ion. Solutions of certain metal sulfides will dissolve sulfur. For example,



Schematic representation of the structure of iron pyrite,  $\text{FeS}_2$ . (Redrawn by permission from A. F. Wells, *Structural Inorganic Chemistry*, The Clarendon Press, Oxford, 1962.)

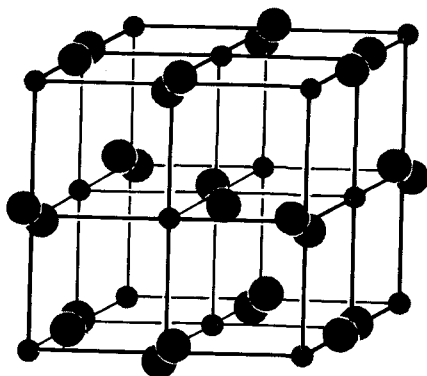
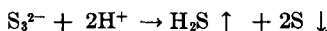


FIG. 22-5

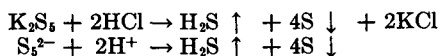
The polysulfide ions range in size from  $\text{S}_2^{2-}$  to  $\text{S}_6^{2-}$ . Large crystals of the most famous polysulfide, the common iron ore *pyrite*,  $\text{FeS}_2$ , look so much like gold that they are called *fool's gold*. Figure 22-5 shows how  $\text{FeS}_2$  crystallizes in a modified NaCl pattern, with S-S pairs occupying the  $\text{Cl}^-$  positions and  $\text{Fe}^{2+}$  ions occupying the  $\text{Na}^+$  positions.

A common laboratory reagent is ammonium polysulfide,  $(\text{NH}_4)_2\text{S}_x$ .<sup>1</sup> It is usually made by dissolving an indefinite amount of sulfur in  $(\text{NH}_4)_2\text{S}$  solution; the  $x$  indicates an unknown number between 2 and 5. Like sulfur, selenium and tellurium also form polyatomic anions,  $\text{Se}_x^{2-}$  and  $\text{Te}_x^{2-}$ , respectively.

The polysulfide ion is decomposed by acid solutions because of the tendency of  $\text{S}^{2-}$  to pick up two  $\text{H}^+$  particles to form  $\text{H}_2\text{S}$ .



When an acid solution is added to a polysulfide solution, finely divided sulfur precipitates and  $\text{H}_2\text{S}$  is evolved:



## OXIDES AND OXY-ACIDS OF SULFUR, SELENIUM, AND TELLURIUM

A number of oxides of the sulfur family are known. Five of sulfur— $\text{SO}$ ,  $\text{S}_2\text{O}_3$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ , and  $\text{SO}_4$ —two of selenium— $\text{SeO}_2$  and  $\text{SeO}_3$ —and three of tellurium— $\text{TeO}$ ,  $\text{TeO}_2$ , and  $\text{TeO}_3$ —have been shown to exist. These many formulas are cited to emphasize the fact that atoms of elements combine in many ratios. In every case, the atoms tend to

<sup>1</sup> The properties of  $\text{NH}_4^+$  salts are so similar to those of certain monovalent metal salts, especially  $\text{K}^+$ , that they are often studied with those metal salts.

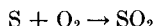


**GROUP VIA:  
THE SULFUR FAMILY**

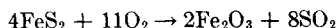
arrange themselves in the most stable way possible under the conditions prevailing at the moment of combination.

Of the sulfur oxides, SO and S<sub>2</sub>O<sub>3</sub> are very unstable and decompose at ordinary room temperature. Of all the sulfur family oxides, only SO<sub>3</sub> and SO<sub>2</sub> have any great use. Both dissolve in water, the former yielding sulfuric acid, H<sub>2</sub>SO<sub>4</sub>, and the latter sulfurous acid, H<sub>2</sub>SO<sub>3</sub>. Note that in the -ic acid the oxidation state is +6, whereas in the -ous acid it is +4.

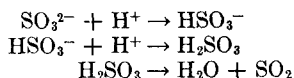
**Sulfur Dioxide.** Sulfur dioxide is the colorless choking gas formed when sulfur burns in air:



and when certain metal sulfides are decomposed by roasting in air:

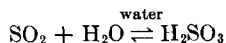


Sulfur dioxide is often prepared for laboratory use by the action of hydrochloric or sulfuric acid on sulfites and bisulfites:

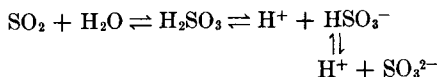


The gas is used as a fungicide, a fumigant (in the form of sulfur candles), and a food preservative. A person who is sensitive to sulfur dioxide may experience a mild choking sensation after eating uncooked dried apricots or peaches that have been treated with the gas. If the fruit is cooked, however, all traces of the sulfur dioxide are driven off.

The structure of the SO<sub>2</sub> molecule is diagramed in Fig. 4-11 and discussed further under "Resonance" in Chap. 17. A typical nonmetal oxide, sulfur dioxide dissolves in and reacts with water to make an acidic solution, sulfurous acid. The compound hydrogen sulfite, H<sub>2</sub>SO<sub>3</sub>, is known only in solutions, because it is too unstable to exist as the pure substance:



**Sulfurous Acid.** Sulfurous acid is a diprotic acid with a moderate tendency to lose one H<sup>+</sup> ion and a very slight tendency to lose two in water. A solution of the acid contains SO<sub>2</sub>, H<sub>2</sub>SO<sub>3</sub>, HSO<sub>3</sub><sup>-</sup>, and SO<sub>3</sub><sup>2-</sup>, as well as the ions of water and water molecules. The equilibria involved in such a solution are



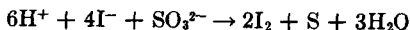
When a solution of sulfurous acid is heated, the sulfur dioxide is driven from the solution. As a result, the reactions toward the left in

the various equilibria are favored. Sulfurous acid is used to bleach delicate textiles, straws, and other natural fibers which chlorine would ruin.

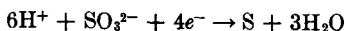
The salts of sulfurous acid are the metal *sulfites* and *acid sulfites*. Examples are sodium sulfite,  $\text{Na}_2\text{SO}_3$ , and potassium acid sulfite,  $\text{KHSO}_3$ . Sodium sulfite is used to remove excess chlorine from wood pulp that has been bleached and to remove oxygen from boiler feed water. Large quantities of calcium bisulfite,  $\text{Ca}(\text{HSO}_3)_2$ , are used in making paper and rayon. The bisulfite solution dissolves the lignin in wood pulp, leaving the purified cellulose.

**OXIDATION AND REDUCTION BY SULFUROUS ACID AND ITS SALTS.** The oxidation state of sulfur in the sulfite ion is +4. Hence it can accept electrons and change to an oxidation state of zero (elemental sulfur) or lose electrons and change to an oxidation state of +6 (sulfate). In the former case, the sulfite is acting as an oxidizing agent; in the latter it is acting as a reducing agent.

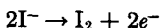
As an oxidizing agent:



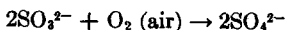
Reduction:



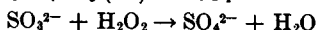
Oxidation:



As a reducing agent:



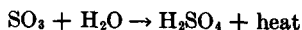
or



When we compare  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  we find that, as in the case of the halogen oxy-acids, the ion that is the more symmetrical is the more stable. As shown in Fig. 22-6, the sulfite ion is an unsymmetrical pyramid with the sulfur exposed at the apex, whereas the sulfate ion is a regular tetrahedron with the sulfur atom nestled inside.

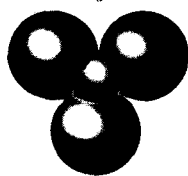
Models of the sulfite ion and the sulfate ion.

**Sulfur Trioxide.** Sulfur trioxide is formed when sulfur dioxide is heated with oxygen in the presence of a catalyst (platinum powder has long been used). At room temperature  $\text{SO}_3$  is a colorless liquid. It has a great affinity for water and combines with it in a highly exothermic reaction:



The important use of sulfur trioxide is in the manufacture of *sulfuric acid*.

the sulfite ion,  
 $\text{SO}_3^{2-}$



top view

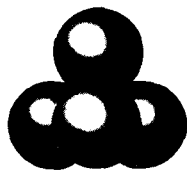


side view

the sulfate ion,  
 $\text{SO}_4^{2-}$



top view



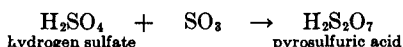
side view

FIG. 22-6

GROUP VIA:  
THE SULFUR FAMILY

**Sulfuric Acid.** Sulfuric acid is most commonly available in the laboratory in a highly concentrated solution that contains about 98 per cent hydrogen sulfate and 2 per cent water. This concentrated acid is a colorless oily liquid with a density of 1.8. When one lifts a large bottle of it, he readily notices that a gallon of it is much heavier than a gallon of water. Although sulfuric acid is very stable toward heat, a dilute solution gradually loses water as it boils; on the other hand, the pure compound loses some sulfur trioxide on boiling. Both dilute and 100 per cent acid change in composition on boiling till they reach the equilibrium constant-boiling mixture of 98.5 per cent  $\text{H}_2\text{SO}_4$  and 1.5 per cent  $\text{H}_2\text{O}$ .

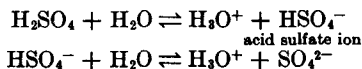
Anhydrous  $\text{H}_2\text{SO}_4$  can be prepared by adding the proper amount of  $\text{SO}_3$  to 98 per cent acid. The pure hydrogen sulfate will combine with more sulfur trioxide to form *pyrosulfuric acid* (or *oleum*, as it is called commercially):



Although it is decomposed at high temperatures, the stability of  $\text{H}_2\text{SO}_4$  is in sharp contrast with the lack of stability of  $\text{H}_2\text{SO}_3$ . Two things should be mentioned in this connection: (1) the reaction of  $\text{SO}_3$  with water is much more exothermic than that of  $\text{SO}_2$  with water, and (2) the  $\text{H}_2\text{SO}_4$  molecule is more symmetrical in structure than the  $\text{H}_2\text{SO}_3$  molecule.

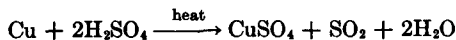
**IMPORTANT PROPERTIES OF SULFURIC ACID.** The fact that such huge quantities of sulfuric acid are used is of course based on the physical and chemical characteristics of the acid and its low price.

It is a *strong acid*, because it reacts easily with water to form the hydronium ion. Because it is a diprotic acid, it loses a second  $\text{H}^+$  after the first is lost.



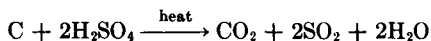
In dilute solution very little of the acid is present as molecular  $\text{H}_2\text{SO}_4$ . Aside from the water, the most abundant entity present is  $\text{H}_3\text{O}^+$ , and there are a relatively large number of  $\text{SO}_4^{2-}$  and  $\text{HSO}_4^-$  ions. Sulfuric acid is the cheapest acid available for dissolving metals and metal oxides, neutralizing bases, and cleaning corroded metal surfaces.

It is an *oxidizing agent*, especially when hot and concentrated. Even such inactive substances as copper and carbon are oxidized when the sulfur in sulfuric acid acquires two electrons and changes its oxidation state from +6 to +4:

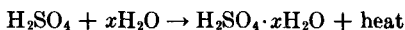


Each copper atom loses two electrons, so that only one sulfate is reduced for each atom of copper.

In the case of carbon, two sulfates per carbon atom must react, because the oxidation state of carbon is changing from 0 to +4:



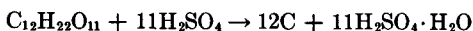
Sulfuric acid is an effective *dehydrating agent* because of its strong affinity for water. The reaction is extremely exothermic:



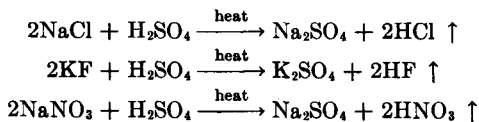
In mixing the concentrated acid with water to make a dilute acid, the acid should always be added slowly to the water, not vice versa. When a little water is added to a large amount of acid, the heat evolved may be sufficient to turn some of the water to steam, causing the hot solution to pop and sputter. If the concentrated acid and water are mixed in an ordinary glass container, the solution can get hot enough so that the vessel cracks; hence it is safer to use a Pyrex glass vessel.

The great amount of heat energy released in this mixing of two liquids indicates that a chemical change is taking place. That this is the case is shown by the fact that definite hydrates have been identified. They have formulas of the type  $\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ , where  $x$  is 1, 2, 3, or 4.

Because of this affinity for water, concentrated sulfuric acid can be used to remove water from other substances, and even to remove hydrogen and oxygen from molecules that do not contain  $\text{H}_2\text{O}$  as such. It will remove most of the water vapor from a wet gas, such as humid air, and will decompose some molecules that contain firmly bound hydrogen and oxygen. In the case of ordinary sugar (sucrose), the residue appears charred, only black carbon being left:



The high boiling point of sulfuric acid is one of its very important properties, because it makes possible the formation of more volatile acids when sulfuric acid is heated with certain salts:



As was pointed out in Chap. 21, pure HBr and HI, though volatile, cannot be made in this way. The hot concentrated sulfuric acid oxidizes iodide ion to elemental iodine,  $\text{I}_2$ , and, to a lesser extent, the bromide ion to elemental bromine,  $\text{Br}_2$ .

**INDUSTRIAL PRODUCTION OF SULFURIC ACID.** The production of sulfuric acid is the largest of all the chemical industries in terms of total output. This useful acid has been manufactured in large quantities for many years; even prior to 1800 it was sold by the ton. About

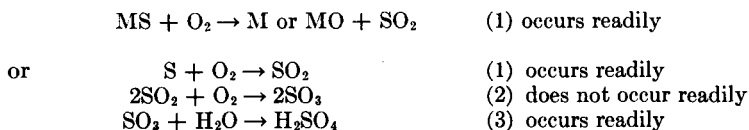
**GROUP VIA:  
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23,500,000 tons per year are now manufactured in the United States.

One-third of the  $\text{H}_2\text{SO}_4$  produced is used in the manufacture of fertilizer, 17 per cent in the manufacture of other chemicals, 10 per cent in the refining of petroleum, and considerable amounts in the manufacture of steel, paints, and cellulose products such as rayon.

There are two methods of making sulfuric acid commercially: the *lead chamber process* and the *contact process*. The first is so named because the reaction chambers are made of sheet lead to prevent corrosion. The second process is so named because the key reaction takes place when two gases come in contact with a catalyst. Although each process has accounted for large percentages of production in recent years, the contact process is responsible for approximately 92 per cent of the sulfuric acid produced at this time.

The chemical reaction of greatest interest in the production of sulfuric acid from sulfur, oxygen, and water is the oxidation of sulfur dioxide to sulfur trioxide. The product formed when either a pyrite or sulfur itself is burned in air is sulfur dioxide,  $\text{SO}_2$ . This gas does not react with additional oxygen during normal combustion; hence the problem is to produce sulfur trioxide,  $\text{SO}_3$ , which can then be dissolved in water, forming sulfuric acid. The reactions are



In the lead chamber process, the oxidation of sulfur dioxide takes place in the presence of oxides of nitrogen by way of a series of complex reactions. In the contact process, sulfur dioxide and oxygen combine directly in a reaction catalyzed by platinum or vanadium pentoxide,  $\text{V}_2\text{O}_5$ . It is this second process that we will discuss in some detail.

In carrying out the reaction



so as to yield the maximum amount of  $\text{SO}_3$ , the temperature and pressure must be considered.

Because the reaction to the right is exothermic, it is favored by a low temperature. The equilibrium constant for the reaction is

$$K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 \times [\text{O}_2]} \quad \text{or} \quad K_p = \frac{p^2_{\text{SO}_3}}{p^2_{\text{SO}_2} \times p_{\text{O}_2}}$$

The variation of this constant with temperature is shown in Fig. 22-7 and Table 22-4.

As indicated by the graph, the conversion of  $\text{SO}_2$  to  $\text{SO}_3$  is practically complete below  $400^\circ\text{C}$ . But if the temperature is too low, the

For the oxidation of sulfur dioxide to sulfur trioxide, the equilibrium constant decreases markedly as the temperature rises.

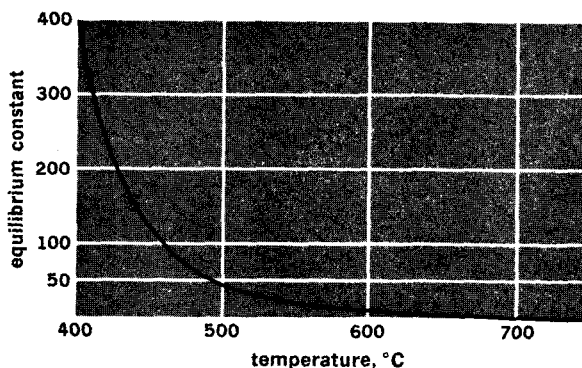


FIG. 22-7

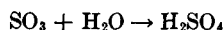
reaction will be so slow that practically no  $\text{SO}_3$  will be formed within any reasonable time. The compromise temperature chosen is about  $450^\circ\text{C}$ . This is low enough to permit most of the sulfur and oxygen to react and high enough to cause the reaction to occur rapidly if a catalyst is present. Because the reaction to the right involves the combining of three molecules to make two, it is favored by a high pressure. However, tests show that the slight increase in the yield of  $\text{SO}_3$  does not justify the increased cost of high-pressure equipment.

*Effect of temperature on equilibrium constant for*  
 $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$

TABLE 22-4

temperature, $^\circ\text{C}$	$K_p$	temperature, $^\circ\text{C}$	$K_p$
400	397	800	0.915
500	48.1	900	0.384
600	9.53	1000	0.184
700	2.63	1100	0.098

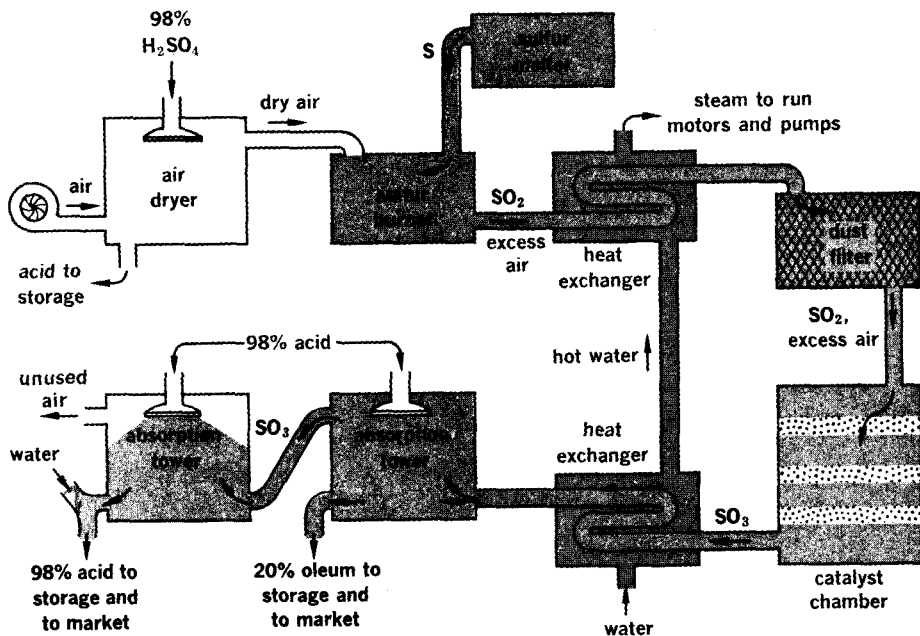
An odd feature is that sulfur trioxide is absorbed much more efficiently by concentrated sulfuric acid than by pure water. Therefore, the trioxide gas is passed through concentrated acid, 98 per cent  $\text{H}_2\text{SO}_4$ . As the gas is absorbed, it reacts with the small amount of water present to form more sulfuric acid.



After all the water is converted to hydrogen sulfate, the acid can absorb more sulfur trioxide to form oleum. The highly concentrated product, which can be diluted to any desired strength by adding water, is the form in which much commercial acid is shipped.

Thus far the discussion seems to indicate that the contact process is carried out as a *batch* operation. This is not the case, for sulfur dioxide is continuously piped into the catalytic chamber, where oxidation is proceeding without pause. The sulfur trioxide also leaves the chamber in a steady stream to be absorbed in the 98 per cent sulfuric acid. The continuous nature of this process is shown diagram-

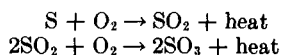
**GROUP VIA:  
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**FIG. 22-8**

A flow sheet showing the main steps in sulfuric acid production by the contact process.

matically in Fig. 22-8. Note the heat exchangers in which steam is generated by the hot gases from the two exothermic reactions:



These boilers are excellent examples of the chemical engineer's ability to kill two birds with one stone. The SO<sub>2</sub> + O<sub>2</sub> mixture and the excess air coming out of the sulfur burner are at 850°C and must be cooled to about 450° before they enter the catalyst chamber. The heat from this mixture is used to generate steam that is used for power. The SO<sub>3</sub> gas, at about 600°C, is cooled to about 200° before being bubbled through the absorption tower filled with 98 per cent acid. The heat from the hot SO<sub>3</sub> is used to heat water in one of the heat exchangers.

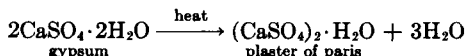
The heat given off by the burning of the sulfur can be harnessed via steam engines to supply power for all the activities of the plant, for example, pumps to move the acid from one tank to another, pumps to move the molten sulfur to the burner, and fans to move the gases from one reaction vessel to another.

The modern sulfuric acid plant is a model of good design and efficiency. Practically all the operations are done by automatic machinery; hence a plant that turns out 100 tons of acid a day may be manned by only a few workmen.

## SULFATES, SELENATES, AND TELLURATES

In compounds where the oxidation state is +6, only the sulfates are common, but selenates and tellurates are known. Because  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SeO}_4$ , and  $\text{H}_2\text{TeO}_4$  are diprotic acids, there are normal salts—for example,  $\text{K}_2\text{SO}_4$  and  $\text{K}_2\text{SeO}_4$ —and acid salts—for example,  $\text{RbHSO}_4$  and  $\text{RbHTeO}_4$ .

Two important mineral sulfates are listed in Table 22-2. Although most sulfates are soluble in water, those of group IIA (Ca, Sr, and Ba) are only slightly soluble. Barium sulfate,  $\text{BaSO}_4$ , is used as a filler to give glazed paper a brilliant whiteness and the desired body. Calcium sulfate forms two familiar hydrates: gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , and plaster of paris,  $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$ . Gypsum is mined in large quantities; a spectacular natural occurrence is the 175,000-acre White Sands National Monument in New Mexico ("Sands" being a misnomer chemically). Plaster of paris, the fundamental ingredient of plaster and stucco, is made by heating gypsum:



When the plaster of paris is mixed with water at room temperature, it slowly picks up enough water of crystallization to turn it back into gypsum. This is the process involved in the setting of plaster of paris.

Among the other useful sulfates are  $\text{CuSO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4$ , and  $\text{Al}_2(\text{SO}_4)_3$ .

**Alums.** The alums are an interesting class of compounds. They are hydrated *double salts*<sup>1</sup> in which two  $\text{SO}_4^{2-}$  anions are combined with one singly charged cation, one triply charged cation, and twelve molecules of water of crystallization. The general formula can be written



$\text{M}^+$  can be  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ag}^+$ ,  $\text{Tl}^+$ , or certain others, and  $\text{M}^{3+}$  can be  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{3+}$ , or certain others. The crystals of one alum are usually isomorphous with the crystals of the others.

Among the most common alums are the aluminum salts (hence the name *alum*).  $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  is used in a certain type of baking powder, and  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  is used in water purification and in fire extinguishers. The latter compound is the common alum of commerce.

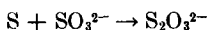
**Thiosulfates.** In a number of compounds a sulfur atom is apparently substituted for an oxygen. In naming these substances the prefix *thio-* (from the Greek *theion*, brimstone) is often used.

<sup>1</sup> All hydrated double salts are not alums. See bromo-carnallite (Table 21-2). The alums are examples of a relatively large class of isomorphous compounds that have a wide range of composition.



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Sulfur reacts with the sulfite ion to form a thiosulfate ion:



Compare the formulas of the sulfate and thiosulfate ions. Sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , is the well-known hypo used by photographers to dissolve silver bromide in developing film. It is also used as a reducing agent to react with excess chlorine in strong bleaching solutions.

## CHAPTER REVIEW

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### *Topics*

Physical and chemical properties of the sulfur family, occurrence, transition temperature, Frasch process, sulfides, selenides, tellurides, polysulfides, pyrites, sulfites, sulfates, contact process, thiosulfates, alums.

### *Exercises*

- Although oxygen is in group VIA, it is not usually thought of as a typical member of the sulfur family. Why?
  - What are some ways in which oxygen does resemble members of the sulfur family?
- In the mining of sulfur superheated water at about  $180^\circ\text{C}$  is pumped down the wells.
  - How is it possible to heat water to such a temperature?
  - Why is not the water heated to a much higher temperature, say  $250^\circ\text{C}$ , in order to melt the sulfur more efficiently?
  - Why is  $180^\circ$  preferable to, say,  $160^\circ$  as a temperature for the water pumped down the wells?
  - What are some other substances that might be mined by a process similar to the Frasch process (with or without heating the water)?
- Would the fact that there are more than 30 allotropes of sulfur indicate that there are a large number of sulfur isotopes also? Explain.
- Discuss in general terms the behavior of the members of the sulfur family with respect to (a) general trends in physical properties and (b) general trends in chemical properties.
  - Because both cesium and selenium are used in light-sensitive devices, can we assume that they have some similar properties?
  - Could copper be substituted for either of the elements above in light-sensitive devices? Explain in each case.
- Account for the difference in the observed ionization energies of sulfur and tellurium (see Table 22-1) on the basis of their atomic structures.
- Work out an  $sp^3d^2$  hybridization diagram for the compound  $\text{SF}_6$ . (See Table 19-9 and Exercise 10, Chap. 21.)

8. Would you expect a resonance hybrid structure in the case of  $\text{SeO}_3$ ? Explain fully.
9. Compare the physical properties of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ , and relate the differences to their molecular structures.
10. Calculate the  $\text{pH}$  of  $0.1N$   $\text{H}_2\text{S}$  and  $\text{H}_2\text{Te}$  solutions.
11. Would you expect the transition from rhombic sulfur to monoclinic to be exo- or endothermic, given that the monoclinic is the preferred form above  $95.5^\circ$ ? If rhombic sulfur is held at  $96^\circ$ , will the transition to the monoclinic form be sudden or gradual? Explain.
12. Plot the melting points versus the molecular weights for  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ , and  $\text{H}_2\text{Te}$ . On the basis of the last three only, what would be the predicted boiling point of  $\text{H}_2\text{O}$ ? How do you account for the difference in the predicted and actual values?
13. a. Calculate the  $\Delta H$ , for the reaction  

$$\text{H}_2\text{S} + \text{Se} \rightarrow \text{H}_2\text{Se} + \text{S}$$
 b. Could you predict the position of equilibrium for this reaction from the calculated  $\Delta H$ ? Explain fully.
14. a. A technique for removing tarnish from silver involves heating silverware in water in an aluminum pan. Write a hypothetical equation for the reaction.  
 b. The removal of the tarnish is speeded greatly by adding an electrolyte to the water, for example, common salt. Explain.
15. Explain how hydrogen sulfide is used in identifying certain cations in chemical analyses.
16. a. Draw electron-dot diagrams of molecules of hydrogen sulfite and hydrogen sulfate.  
 b. By a consideration of oxidation states of sulfur and corresponding electron pair shifts, show how the relative strengths of sulfurous and sulfuric acids can be correlated with their electron-dot diagrams.
17. Write an equation for the reaction of chlorine plus selenious acid in water to yield selenic acid and hydrochloric acid.
18. Write the equations for the ionization of hydroselenic acid. Write the expressions for  $K_{i1}$  and  $K_{i2}$ . Would you expect  $K_{i2}$  to be larger than  $K_{i1}$ ? Why? Would you expect  $K_{i1}$  to be large or small as compared with  $\text{H}_2\text{S}$ ? Why?
19. Calculate the volume at STP of hydrogen sulfide necessary to precipitate the copper in 200 ml of 1 molar copper(II) sulfate. (Assume 100 per cent efficiency.)
20. Draw a simple diagram of a mechanical refrigeration system and show how sulfur dioxide might be used in it.
21.  $\text{H}_2\text{SO}_4$  is an unstable compound, decomposing readily, whereas  $\text{H}_2\text{SO}_3$  is one of the most stable acids known. What similar behavior was mentioned in discussing the potassium salts of chlorine oxy-ions? Can we account for these similar cases on the basis of similar principles?

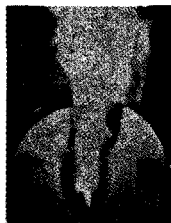
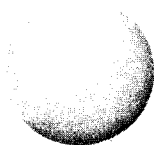
GROUP VIA:  
THE SULFUR FAMILY

22. Although silver is well below hydrogen in oxidation potential, concentrated sulfuric acid will attack it. Explain and write a possible equation for the reaction.
23. Sulfuric acid has long been used in preparing other acids from their salts. Give examples. What physical property is important here?
24. Calculate the weight of  $\text{FeS}_2$  required to make 200 lb of 60 per cent sulfuric acid. Assume 90 per cent efficiency for the process.
25. Sulfurous acid may act as either an oxidizing agent or a reducing agent, but sulfuric acid acts only as an oxidizing agent. Why?
26. Consider the oxidation of sulfur dioxide as described in Table 22-4.
  - a. Discuss whether  $\Delta H_r$  for the reaction can be correlated with  $K_p$  in a straightforward way.
  - b. Assuming that  $\Delta H_r$  is relatively constant, what is the sign of  $\Delta S_r$  that is indicated by the observed change in  $K_p$  with temperature?
  - c. What does the sign of  $\Delta S_r$  tell us about the overall order versus disorder of the reactants and products?
27. Make a rough diagram of a heat exchanger and label to show how it could be used in a chemical plant. Do you think something similar is used in a home furnace fired by coal or gas?
28. When a sulfuric acid plant like that diagramed in Fig. 22-8 is in production, where does the 98 per cent  $\text{H}_2\text{SO}_4$  used in the air dryer come from? If it were diluted to 96 per cent by drying the incoming air, how might the concentration of the acid used for drying be raised to 98 per cent again?
29. Alums generally taste sour. Explain, giving an equation.
30. Baking powders may consist of bicarbonate of soda,  $\text{NaHCO}_3$ , and, as an acid component,  $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  (an alum). Explain how this substance is able to act as an acid when added to water, and how it liberates carbon dioxide from the bicarbonate of soda. Write the equations.
31. "The reason your plaster of paris did not set was because it was too wet." What do you think of this opinion?
32. When a solution of sodium thiosulfate is used to dissolve silver bromide, one of the products is the complex ion  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ . Write an ionic equation for the reaction.
33. What weight of 98.5 per cent sulfuric acid is required to neutralize 200 ml of a 5.2 *M* sodium hydroxide solution? What weight of pure  $\text{NaOH}$  is involved?
34.
  - a. Name two sulfur-containing minerals in which sulfur is in a reduced state and two in which it is in an oxidized state.
  - b. Name elements that occur in nature (1) only in the reduced state, (2) only in the oxidized state, (3) usually in the elemental state. Compare sulfur with these elements on the basis of chemical reactivity.
35. When thiosulfate ions react in an oxidation-reduction reaction with chlorine in aqueous solution, sulfate ions are among the products. Write balanced equations for the reduction, oxidation, and overall ionic reactions.

36. Classify each of the following species into one of the following categories —(a) act only as oxidizing agents; (b) act only as reducing agents; (c) may act as oxidizing or reducing agents:  
 $\text{Cl}^0$ ,  $\text{S}^{6+}$ ,  $\text{Se}^{4+}$ ,  $\text{S}^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Cl}^{5+}$ ,  $\text{Cl}^{1+}$ ,  $\text{S}^{4+}$ ,  $\text{S}^0$ ,  $\text{Cl}^+$ ,  $\text{Br}^-$ ,  $\text{F}^0$ ,  $\text{F}^-$ ,  $\text{Te}^{2-}$
37. Write balanced equations showing the action of sulfuric acid as (a) an acid; (b) a dehydrating agent; (c) an oxidizing agent.
38. List all the ions present in the solution that results when  $\text{H}_2\text{SO}_4$  is added to water and indicate which is the most abundant ion and which is the least abundant ion.
39. Why might sulfurous acid be preferable to chlorine as a bleach?
40. Write equations for the following reactions:
  - a. Silver and sulfur
  - b. Copper and selenium
  - c. Hydrogen and tellurium
  - d. Formation of selenious acid from its elements
  - e. Formation of sulfur monochloride
  - f. Roasting of chalcopyrite in air
  - g. Solutions of barium polysulfide and sulfuric acid (identify precipitates)
  - h. Formation of a sodium polyselenide solution
  - i. Oxidation-reduction reaction of sulfurous and hydrosulfuric acids
  - j. Bromine and sulfurous acid
  - k. Hot, concentrated sulfuric acid and potassium chloride
  - l. Hot, concentrated sulfuric acid and potassium iodide
41. In Table 22-3 the enthalpy of formation for  $\text{H}_2\text{O}$  is for the production of the liquid state, but for the other compounds it is for the gaseous state. Is it logical to report the data in this way? How does this affect the relation of the values?

### SUPPLEMENTARY READING

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- Tuller, W. N.: *The Sulfur Data Book*, McGraw-Hill Book Company, Inc., New York, 1954, sec. 1.

**GROUP VA:****THE NITROGEN FAMILY****N 0.74 Å****P 1.10****As 1.21****Sb 1.41****Bi 1.52****FIG. 23-1**

The elements in group VA of the periodic table constitute the nitrogen family. These elements, each of which has five electrons ( $s^2p^3$ ) in its outside main energy level, are nitrogen, phosphorus, arsenic, antimony, and bismuth. They are similar to one another in some respects but are more noted for their differences. The stepwise change from nonmetallic to metallic character within a group is more clearly evident in the nitrogen family than in any other.

In group VIA oxygen was considered apart from the other elements because of its very different physical and chemical properties. Similarly, nitrogen is unlike the other group VA elements.

**PROPERTIES OF THE NITROGEN FAMILY****PHYSICAL PROPERTIES**

A few of the important physical properties of the nitrogen family are listed in Table 23-1. The trend from nonmetal to metal is quite evident. (1) Both antimony and bismuth have the luster of metals on freshly broken surfaces; (2) the ionization energy values reveal that

The relative sizes of atoms in the nitrogen family.

nitrogen holds onto its outside electrons most strongly, bismuth least strongly; (3) the electronegativities show that nitrogen has a high electron affinity and that the affinity decreases down the family to antimony (and presumably bismuth). Measurements of the electrical conductivity (not included in the table) show that it increases from nitrogen to bismuth.

The regular trend in size is apparent in the group, the size increasing steadily as the atomic number increases. An interesting comparison of the radii of atoms in different combinations can be made from Table 23-1. Note how large the radius is for a particle in the  $-3$  oxidation state and how much smaller it is for the  $+5$  oxidation state. The ideal covalent radius is intermediate in value (an electron pair is equally shared with another atom). Figure 23-1 shows diagrams of the five atoms drawn to scale on the basis of their covalent radii.

*Physical properties of the nitrogen family*

**TABLE 23-1**

	nitrogen N	phosphorus P	arsenic As	antimony Sb	bismuth Bi
appearance at room temperature	colorless gas	waxy white, red (violet), or black solid	steel-gray solid	blue-white solid, metallic luster	pinkish white solid, metallic luster
common molecular formula	N <sub>2</sub>	P <sub>4</sub>	As <sub>4</sub>	Sb	Bi
melting point, °C	—210	44* 592†	814 (36 atm)	630	271
boiling point, °C	—196	280	610 (sublimes)	1440	1420
ionization energy, ev	14.5 (334 kcal)	11.0 (254 kcal)	9.81 (226 kcal)	8.64 (199 kcal)	7.29 (168 kcal)
covalent radius, Å	0.74	1.10	1.21	1.41	1.52
crystal radius (X <sup>3-</sup> ), Å	1.71	2.12	2.22	2.45	
crystal radius (X <sup>5+</sup> ), Å	0.11	0.34	0.47	0.62	0.74
electronic structure	2,5	2,8,5	2,8,18,5	2,8,18,18,5	2,8,18,32,18,5
electronegativity	3.0	2.1	2.0	1.8	

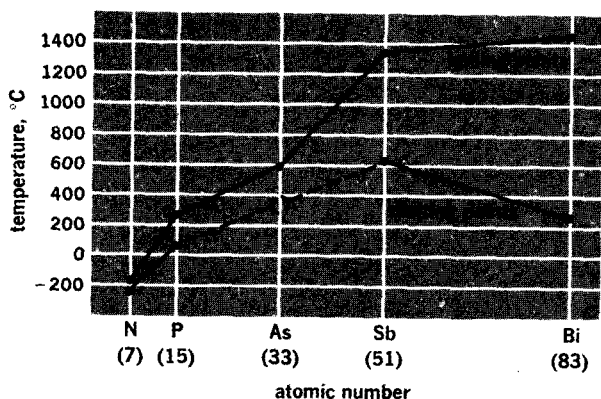
\*White phosphorus.

†Red phosphorus.

All the elements except nitrogen are solids. The melting and boiling points of these elements are worthy of special attention; they are plotted in Fig. 23-2. Note the slight difference in the melting and boiling points for nitrogen. It has a liquid range of only 14°, whereas bismuth has a liquid range of 1149°. The melting point for bismuth (271°) is relatively low for a metal.

Note also, in Table 23-1, the tremendous difference in the melting point for the white and red forms of phosphorus. Because both are pure phosphorus, it is evident that this difference is due to the structure of the two. White phosphorus is made up of discrete P<sub>4</sub> molecules attracted to one another by weak van der Waals forces, whereas the red (or violet) form is crystallized in layers of tightly bound atoms (Fig. 23-3). In the P<sub>4</sub> molecule the bonds arise from the interaction of 3p orbitals, with the bonding orbitals bent outward from the line joining the centers of each pair of atoms. White phosphorus is very

GROUP VA:  
THE NITROGEN FAMILY



Differences between the melting and boiling points for the members of the nitrogen family. (The melting point for arsenic is not plotted, since arsenic sublimes rather than melts when heated at atmospheric pressure.)

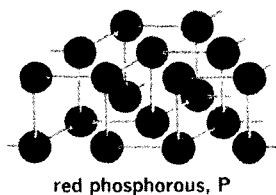
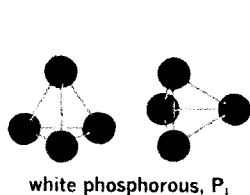
FIG. 23-2

active chemically, is soluble in carbon disulfide, and is poisonous; red phosphorus has none of these properties.

Actually, solid phosphorus, arsenic, and antimony each have at least two allotropic (or polymorphic) modifications—a nonmetallic form of low density and a dense, more closely packed metallic form. Solid nitrogen has only a nonmetallic structure, and solid bismuth has only a metallic one.

The behavior of arsenic is typical of substances (for example,  $\text{CO}_2$ ) that cannot exist as liquids at atmospheric pressure. When heated, arsenic does not melt; instead, it passes directly from the solid state into the vapor state (sublimes). If heated under pressure it can exist in the liquid state.

The molecular formulas  $\text{N}_2$ ,  $\text{P}_4$ ,  $\text{As}_4$ ,  $\text{Sb}_4$ , and  $\text{Bi}_4$  are informative. Of all the elements, only the nonmetals tend to form simple polyatomic molecules.<sup>1</sup> The symbols Sb and Bi, lacking subscripts, indicate that these elements crystallize like metals, with the single atom acting as an independent unit.



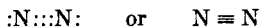
The molecular structure of two polymorphic forms of phosphorus. (Redrawn by permission from A. F. Wells, *Structural Inorganic Chemistry*, The Clarendon Press, Oxford, 1962.)

FIG. 23-3

<sup>1</sup> There are three solid non-metals which do not form simple polyatomic molecules under ordinary conditions, but rather crystallize in indefinitely large polyatomic crystals. Their symbols indicate independent atoms—boron, B, carbon, C, and silicon, Si.

## CHEMICAL PROPERTIES

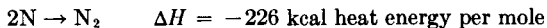
**Reactivity.** Perhaps the most striking chemical property of the nitrogen family (indeed one of the most striking chemical properties of any of the elements) is the inactivity of elemental nitrogen. With an electronegativity of 3.0 (equal to chlorine, exceeded only by oxygen and fluorine), nitrogen should be one of the most active of all elements. Actually, it resists combination with other atoms as a result of the great affinity that one nitrogen atom has for another. In molecules of elemental nitrogen,  $N_2$ , the two nitrogen atoms share three pairs of electrons. Such a bond is called a **triple covalent bond**, or more simply, a **triple bond**:



Molecular nitrogen can be decomposed by a very high-voltage electrical discharge:



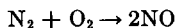
The same amount of energy is liberated when the atoms recombine:



These two reactions are the basis for an atomic nitrogen torch which is used to generate a very high temperature flame. A stream of nitrogen is directed between the poles of an electric arc that dissociates the  $N_2$  molecules into atoms. As the gaseous atoms immediately recombine to form molecules, heat energy is released in the form of radiant energy and hot gas. There is also an atomic hydrogen torch that operates on the same principle. Such flames are useful because of their high temperatures and because they permit use of oxygen-free flames.

The inactivity of nitrogen is apparent in many common processes. In the changes involved in combustion, fermentation, decay, and the respiration of animals it is the oxygen of the air, not the nitrogen, that participates. When air is being used by a furnace or an automobile engine, almost all the nitrogen (78 per cent of the air) passes unchanged through the furnace or engine and is returned to the atmosphere. (In automobile exhaust fumes there can be slight traces of nitrogen oxides. These acidic oxides contribute to air pollution, especially in crowded cities.)

Under extreme temperatures and pressures or in the presence of catalysts, nitrogen does react with other elements. For example, nitrogen and oxygen combine when a high-voltage spark passes through a mixture of the two:



This reaction probably follows a *chain mechanism* similar to that described for hydrogen and chlorine in Chap. 21. The spark dissociates



GROUP VA:  
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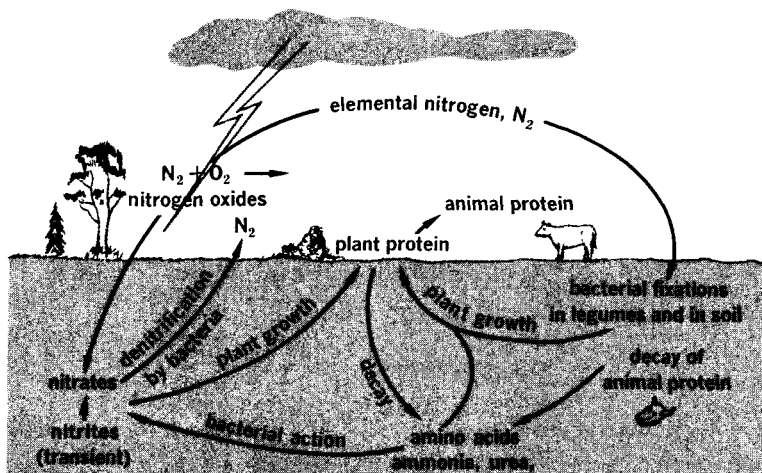
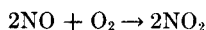


FIG. 23-4

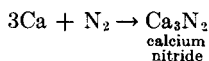
The nitrogen cycle in nature.

some  $O_2$  and  $N_2$  molecules into atoms to initiate the chain. In a similar fashion, some of the nitrogen and oxygen in the path of a bolt of lightning during thunderstorms is converted into nitric oxide ( $NO$ ). The nitric oxide then reacts with more oxygen of the air to form nitrogen dioxide:



The nitrogen dioxide produced during lightning storms dissolves in rain water, forming a very dilute solution of nitric acid. In this way, a considerable amount of the inactive elemental nitrogen of the air is converted into nitrogen compounds and deposited in the soil for use by plants as food. (See Fig. 23-4.) This is one of nature's **nitrogen fixation processes**.<sup>1</sup> It is estimated that a region with moderate rainfall receives 5 to 7 lb of nitrogen (as  $HNO_3$ ) per acre per year.

With some of the very active metals, nitrogen reacts and forms *ionic nitrides*:

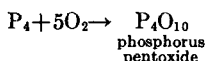
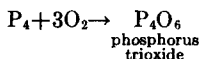


Similar reactions occur with such metals as magnesium, lithium, and aluminum.

In contrast to nitrogen with its slight activity, phosphorus is very

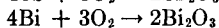
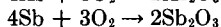
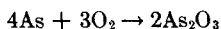
<sup>1</sup> Nitrogen fixation is any process in which elemental nitrogen reacts to form a compound, for example, a fertilizer. Artificial fixation of nitrogen by the direct union of nitrogen and oxygen has been commercially developed in some areas where electric power is cheap. Nitrogen and oxygen are blown through an electric arc; the resulting  $NO$  is oxidized to  $NO_2$  and then combined with water to make nitric acid.

active. It burns readily in air, forming either the trioxide or the pentoxide,<sup>1</sup> depending on the availability of oxygen:

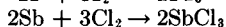
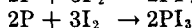
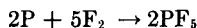


The kindling temperature of white phosphorus is about room temperature; hence it tends to ignite spontaneously. The kindling temperature of red phosphorus is much higher. Phosphorus reacts vigorously with the halogens to form such compounds as  $\text{PCl}_3$ ,  $\text{PBr}_3$ , and  $\text{PI}_3$ .

Arsenic, antimony, and bismuth are not affected by oxygen at ordinary temperatures. At elevated temperatures, however, each burns to the trioxide. For simplicity, P and As are frequently used in equations, rather than  $\text{P}_4$  and  $\text{As}_4$ :



Halogens combine directly with the VA elements, except nitrogen, to form either the pentahalides or the trihalides. Examples are



**Oxidation State.** Compounds are known in which one or more of the nitrogen family have oxidation states of  $-3$ ,  $-2$ ,  $-1$ ,  $+1$ ,  $+2$ ,  $+3$ ,  $+4$ , and  $+5$ , but the common ones are  $-3$ ,  $+3$ , and  $+5$ . The three common states are explained nicely on the basis of the use in bonding of the three  $p$  electrons or the use of both the three  $p$  electrons and the two  $s$  electrons. Compounds of the various oxidation states are listed in Tables 23-3 and 23-4.

**Trend from Nonmetals to Metals.** We have observed that the physical properties of the nitrogen family change from those characteristic of nonmetals to those characteristic of metals as one proceeds down the family. The chemical properties also show this important trend.

**STABILITY OF HYDRIDES.** The tendency to acquire electrons and become negative ions, or to be in a negative oxidation state, is characteristic of nonmetals. In the nitrogen family, nitrogen has the greatest tendency to have an oxidation state of  $-3$ , but bismuth does not form stable compounds in which its oxidation state is  $-3$ . The

<sup>1</sup> The terms "trioxide" and "pentoxide" are holdovers from the days when the formulas for these compounds were written as  $\text{P}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ , respectively. The modern names phosphorus(III) oxide and phosphorus(V) oxide are used more and more in texts, but the old names, like those of many other compounds, are slow to disappear.

**GROUP VA:  
THE NITROGEN FAMILY**

hydrogen compounds illustrate this trend very well, as shown by the data in Table 23-2. Only the nitrogen compound,  $\text{NH}_3$ , is stable enough to be made by the direct union of the elements. Note also that arsine,  $\text{AsH}_3$ , and stibine,  $\text{SbH}_3$ , are endothermic compounds, almost a sure sign of instability.

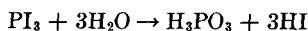
**TABLE 23-2** *Hydrogen compounds of nitrogen family*

name	formula	$\Delta H$ per mole for	remarks
		$\text{E} + \frac{3}{2}\text{H}_2 \rightarrow \text{EH}_3$ , kcal	
ammonia	$\text{NH}_3$	-11.0	stable in air; decomposes when strongly heated
phosphine	$\text{PH}_3$	- 1.9	bursts into flame in air; easily decomposed by heat
arsine	$\text{AsH}_3$	+36.7	easily decomposed by heat
stibine	$\text{SbH}_3$	+34 (?)	decomposes explosively when heated
bismuthine	$\text{BiH}_3$	(?)	decomposes spontaneously at room temperature

The same trend from nonmetal to metal behavior was indicated in group VIA by the decrease in stability of the compounds  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ , and  $\text{H}_2\text{Te}$ .

**TENDENCY TO FORM SIMPLE CATIONS.** Bismuth has the greatest tendency to lose electrons and attain the +3 state. None of the five elements forms highly ionic compounds with nonmetals, but bismuth forms some ionic-covalent compounds. For example, liquid  $\text{PCl}_3$  is a nonconductor of electric current, whereas liquid  $\text{BiCl}_3$  is a conductor.

Furthermore, only antimony and bismuth form simple metallike cations in water solutions; these are  $\text{Sb}^{3+}$  and  $\text{Bi}^{3+}$ , respectively. Nonmetals have too great an attraction for electrons to exist as positive ions in a water solution. Such possible ions evidently react with water (hydrolyze) by attracting an electron pair of a water molecule. The overall hydrolysis equation for phosphorus is



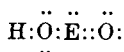
Of the +3 compounds in group VA,  $\text{Bi}^{3+}$  compounds hydrolyze least because  $\text{Bi}^{3+}$  has the least attraction for electrons of all the +3 ions.

The +5 oxidation state is shown by all the nitrogen family elements. Even so, the simple pentavalent cations, including bismuth, are unknown, because a particle with a charge of +5 will attract electron pairs and form covalent bonds with practically any other atom or molecule it touches. For example, isolated  $\text{N}^{5+}$  is not known, but  $\text{NO}_3^-$  is;  $\text{P}^{5+}$  is not known, but  $\text{PCl}_5$  is.

The most important +5 compounds are the nitrates,  $\text{NO}_3^-$ , and the phosphates,  $\text{PO}_4^{3-}$ .

**ACID-BASE-FORMING TENDENCIES.** The elements in group VA form series of compounds that are analogues of nitrous acid,  $\text{HNO}_2$ , and of nitric acid,  $\text{HNO}_3$ . As we proceed down either series, there is a decreasing tendency for the compound to act as an acid and an increasing tendency for it to act as a base. This behavior can be attributed to the gradual change down the family from a nonmetallic element (nitrogen), with a considerable attraction for electrons, to a metallic element (bismuth), with a much smaller attraction for electrons.

If E stands for any of the five elements, we can write the general formula for the  $\text{HNO}_2$  series as  $\text{HEO}_2$  and the electronic formula as



When E is an element that has a strong attraction for electrons, that is, a nonmetallic element, electrons are attracted away from the proton, so that it is readily donated to proton-attracting groups; that is,  $\text{HEO}_2$  tends to act as an acid:

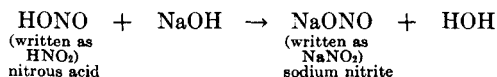


When E is weakly electronegative, that is, a metallic element,  $\text{HEO}_2$  tends to act as a base:

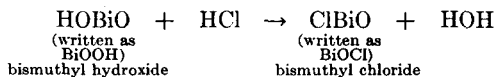


Experiments show that, among the  $\text{HEO}_2$  compounds of the nitrogen family, nitrous acid is the strongest acid (although it is not very strong); phosphorous acid is next in strength; arsenious acid is weakly acidic and can even act as a base; antimonous acid has no pronounced acidic or basic properties, although it can act as either under the proper conditions; and bismuthyl hydroxide is a weak base. The following equations illustrate some acid-base reactions of the  $\text{HEO}_2$  compounds:

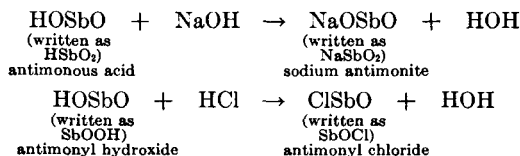
As an acid:



As a base:



As either an acid or a base:



**GROUP VA:**  
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Hydroxides that can act as either acids or bases are called *amphoteric hydroxides*.  $\text{HAsO}_2$  and  $\text{HSbO}_2$  are examples.

**OCCURRENCE**

The most abundant of the elements in the nitrogen family is phosphorus; it ranks tenth among the elements in the earth's crust, 0.12 per cent by weight. The other elements are not abundant on a

**TABLE 23-3**     *Minerals of the nitrogen family*

name	formula	oxidation state	mineral name
sodium nitrate	$\text{NaNO}_3$	5	Chilean nitrate
calcium phosphate	$\text{Ca}_3(\text{PO}_4)_2$	5	phosphorite
calcium chlorofluophosphate	$\text{Ca}_5(\text{Cl}, \text{F})(\text{PO}_4)_3$	5	apatite*
iron arsenide sulfide	$\text{FeAsS}$	?	arsenical pyrites
arsenic(III) sulfide	$\text{As}_2\text{S}_3$	3	orpiment
arsenic(II) sulfide	$\text{As}_2\text{S}_2$	2	realgar
antimony sulfide	$\text{Sb}_2\text{S}_3$	3	stibnite
antimony oxide	$\text{Sb}_2\text{O}_3$	3	senarmonite
bismuth sulfide	$\text{Bi}_2\text{S}_3$	3	bismuthite
bismuth oxide monohydrate	$\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$	3	bismite

\*In apatite,  $\text{Cl}^-$  and  $\text{F}^-$  ions replace each other in all proportions by isomorphic substitution. The fact that teeth are composed in part of a similar substance is the basis for the fluoridation of water. The proper amount of  $\text{F}^-$  ions in the water apparently promotes the formation of teeth that are especially resistant to decay by increasing the  $\text{F}^-$  content and decreasing the  $\text{Cl}^-$  content of the enamel.

weight basis, but they are not rare by any means. Elemental nitrogen,  $\text{N}_2$ , makes up 78 per cent of the atmosphere, and nitrogen compounds (especially proteins) are constituents of all living things. Arsenic, antimony, and bismuth are found in both the elemental and combined form in nature and are easily prepared from their compounds. Only phosphorus is so active that it is found in nature only in compounds.

Common minerals of the family are listed in Table 23-3. Sodium nitrate,  $\text{NaNO}_3$ , and calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , are both used in the manufacture of fertilizers. Phosphorus, like nitrogen, is essential to the growth of living things; phosphorus compounds are found in the protoplasm of cells. Note that the most common minerals of the elements of a metallic character, arsenic, antimony, and bismuth, are the *sulfides* and *oxides*.

**PREPARATION AND USES OF THE NITROGEN FAMILY**

**NITROGEN**

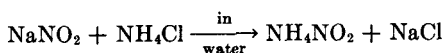
Nitrogen is produced most easily by separating it from the atmosphere. Air is compressed and cooled till it is liquid and then allowed to

boil; the nitrogen is separated by fractional distillation. The nitrogen produced in this way is not absolutely pure, for it contains small amounts of other gases such as oxygen and the noble elements.

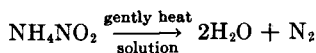
Very pure nitrogen can be prepared by the thermal decomposition of an unstable nitrogen compound. Many nitrogen compounds are easily broken down, because the bonds that hold the molecule together are not so strong as the  $\text{N}\equiv\text{N}$  bond, and therefore the nitrogen atoms tend to break away to form nitrogen molecules,  $\text{N}_2$ .

Ammonium nitrite is often used as a laboratory source of nitrogen gas; this compound is so unstable that it is best to make it as needed from two more stable compounds:

Step 1



Step 2

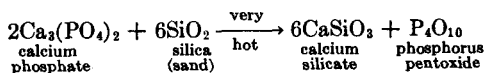


The decomposition of such compounds is the result of the tendency for atoms to group themselves together in the most stable structures possible. Under ordinary conditions  $\text{N}_2$  is the most stable structure nitrogen atoms can attain.

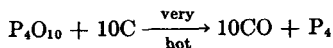
Nitrogen gas is used in huge quantities for the production of ammonia,  $\text{NH}_3$ . Smaller amounts are used in the hardening of steel and in chambers where an inactive atmosphere is desired. (Such chambers range from large rooms, to laboratory hoods, to electric light bulbs.) Liquid nitrogen in a Dewar vessel can be used as a refrigerant, because it boils at  $-196^\circ\text{C}$ .

## PHOSPHORUS

Phosphorus is produced on a large scale by a reaction between a phosphate mineral, coke, and sand. A number of complex reactions undoubtedly occur in steps, but the process can be summarized as follows:



then



As the  $\text{P}_4\text{O}_{10}$  vapor rises through the mixture, it comes in contact with hot carbon. The second reaction tends to occur because the carbon forms a stronger bond with oxygen than phosphorus does. Carbon acts as a reducing agent here as phosphorus vapor is formed.

**GROUP VA:  
THE NITROGEN FAMILY**

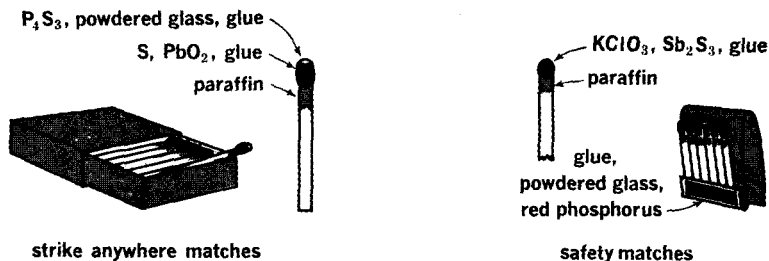


FIG. 23-5

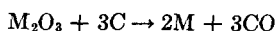
The composition of two types of matches.

The  $P_4$  is separated from the gaseous CO by running the mixture through cool pipes in which liquid phosphorus condenses. (Great care must be taken to protect personnel against any leakage of CO and  $P_4$  vapors.)

Elemental phosphorus is used in the manufacture of certain widely used bronze alloys, in the production of phosphoric acid,  $H_3PO_4$ , and in the manufacture of matches (Fig. 23-5), smoke bomb mixes, tracer bullets, and pest poisons.

## OTHER ELEMENTS

*Arsenic, antimony, and bismuth* are often produced by reducing the appropriate oxide with carbon. This type of reaction is something of a classic, for it has been used for centuries to separate various metals from their ores. If M stands for As, Sb, or Bi, the reaction proceeds thus:



These three nitrogen family elements are used mainly mixed with metals to make alloys with certain desirable properties. A trace of arsenic is added to lead shot to make the lead harder and its surface tension higher.<sup>1</sup> Antimony is used in alloys to dilute more expensive metals, such as lead and tin. Antimony alloys do not have great tensile strength, but they can be used for cheap castings such as white metal (small toys and decorations). Babbitt, an alloy of antimony, is used in bearings.

Bismuth and antimony alloys tend to expand when they solidify;<sup>2</sup> hence they are useful in making good castings. The expanding metal fills even the finest details of the mold. Bismuth is a component of some alloys with very low melting points that are used as safety plugs in steam boilers and in automatic fire-control sprinkler systems.

<sup>1</sup> Lead shot are formed by allowing tiny drops of molten lead to fall in air; the greater the surface tension of the liquid, the more nearly spherical the droplet before it solidifies.

<sup>2</sup> The water-ice transformation is the most familiar example of this rare phenomenon.

## REPRESENTATIVE COMPOUNDS OF THE NITROGEN FAMILY

Nitrogen forms a number of simple compounds in which its oxidation states range from  $-3$  to  $+5$  (see Table 23-4).

### *Oxidation states of nitrogen*

TABLE 23-4

oxidation			oxidation		
name	formula	state	name	formula	state
ammonia	$\text{NH}_3$	$-3$	nitric oxide	$\text{NO}$	$+2$
hydrazine	$\text{N}_2\text{H}_4$	$-2$	nitrogen trioxide	$\text{N}_2\text{O}_3$	$+3$
hydroxylamine	$\text{NH}_2\text{OH}$	$-1$	nitrogen dioxide	$\text{NO}_2$	$+4$
nitrogen	$\text{N}_2$	$0$	nitrogen		
nitrous oxide	$\text{N}_2\text{O}$	$+1$	pentoxide	$\text{N}_2\text{O}_5$	$+5$

### AMMONIA

Ammonia,  $\text{NH}_3$ , is a common, extremely useful compound that is produced commercially in huge quantities by the direct union of nitrogen and hydrogen. It is made in nature by the decay of the proteins in the bodies of plants and animals (see the nitrogen cycle, Fig. 23-4). Ammonia is used as a fertilizer, a refrigeration gas, and a solvent. It is a raw material in the manufacture of ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ , nitric acid,  $\text{HNO}_3$ , and ammonium nitrate,  $\text{NH}_4\text{NO}_3$ .

Dissolved in water it forms a solution known as *ammonium hydroxide* or *ammonia water*. This weakly basic solution is used as a fertilizer, as a neutralizer of acid solutions, and as a cleansing agent (household ammonia). The odor of ammonia rising from the solution<sup>1</sup> reveals that the ammonia water is not very stable; indeed, the ammonia can be completely driven out of the water by boiling.

The great solubility of ammonia in water is unusual, about 700 liters of the gas dissolving in 1 liter of water under room conditions. The attraction of water for ammonia is so great that, if a little water is introduced into a chamber filled with the gas, a partial vacuum will result. This is the basis of a demonstration known as the ammonia "fountain," similar to the hydrogen chloride "fountain" shown in Fig. 21-8. (Since ammonia is a base, the color change is opposite to that shown in the figure for the acidic hydrogen chloride.)

The chemistry of ammonia is worthy of close attention, for it is very instructive, and much of it can be interpreted in terms of the theoretical properties of atoms and molecules. The  $\text{NH}_3$  molecule is a pyramid with the nitrogen at the apex, as shown in Fig. 23-6. The molecule can be considered an incomplete tetrahedron (N at the center) with the two unused electrons held on the side away from the three hydrogen

<sup>1</sup> A whiff of ammonia water is sometimes used to revive a person who has fainted.



GROUP VA:  
THE NITROGEN FAMILY

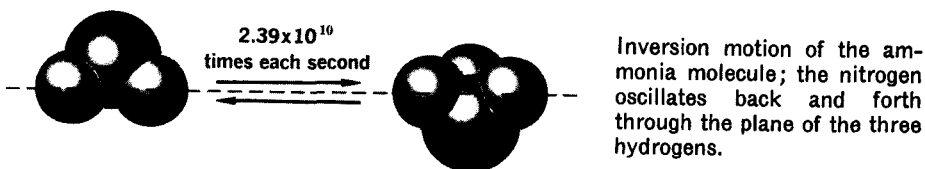


FIG. 23-6

atoms. Like the  $\text{H}:\ddot{\text{O}}:$  molecule, the  $\text{H}:\ddot{\text{N}}:\text{H}$  molecule is a polar molecule, because of the unsymmetrical distribution of positive and negative charges.

In addition to the vibration and rotation motions that we would expect, the  $\text{NH}_3$  molecule has the unusual and fascinating motion of *inversion*, as pictured in Fig. 23-6. In spite of the rapidity with which it turns itself inside out, the ammonia molecule still acts as a polar molecule and has a dipole moment. This is because the rate of inversion, although extremely fast, is considerably slower than the rate of rotation, so that the molecules have time to become aligned in an electric field between inversions. If the rate of inversion were sufficiently great, ammonia molecules presumably would be nonpolar.

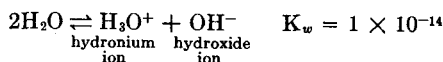
Ammonia is more like water than is any other compound. The physical properties of the two liquids are compared in Table 24-5. Below  $-33^\circ\text{C}$  ammonia is a colorless liquid. It is an excellent solvent

TABLE 23-5 *Comparison of physical properties of ammonia and water*

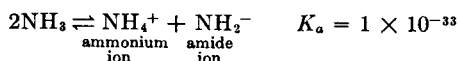
formula	$\text{NH}_3$	$\text{H}_2\text{O}$	specific heat, cal/g	1.07	1.00
melting point, $^\circ\text{C}$	-77	0	heat of fusion, cal/g	81.5	79.7
boiling point, $^\circ\text{C}$	-33.4	100	heat of vaporization, cal/g	327.1	539.6
critical temperature, $^\circ\text{C}$	132.5	374	relative viscosity	0.24	1

for most of the compounds that dissolve in water. Both ionic and covalent compounds dissolve in ammonia, and chemical reactions involving precipitations, gas evolution, electrolysis, oxidation-reduction, and acids and bases can be carried out.

Just as water ionizes slightly,



so liquid ammonia does likewise:



Investigation of the chemistry of ammonia has revealed the existence of a whole system of nitrogen compounds that are analogous to the oxygen compounds formed in water solutions. A number of

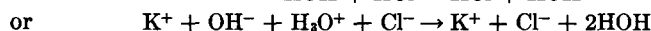
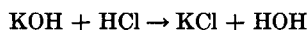
*Water system compounds and their ammonia analogues*

TABLE 23-6

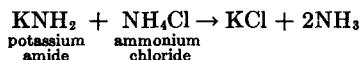
type of compound	water system	ammonia system
acid	$\text{H}_3\text{O}^+ \text{Cl}^-$	$\text{NH}_4^+ \text{Cl}^-$
base	$\text{Na}^+ \text{OH}^-$	$\text{Na}^+ \text{NH}_2^-$
salt	$\text{Na}^+ \text{Cl}^-$	$\text{Na}^+ \text{Cl}^-$
oxide or nitride	$\text{CaO}$	$\text{Ca}_3\text{N}_2$
solvate	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	$\text{CaCl}_2 \cdot 6\text{NH}_3$

familiar water compounds and their ammonia analogues are listed in Table 23-6.

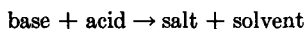
In water the reaction between a base and an acid can be written as



In ammonia the analogous reactions are



In both cases the reaction is



The thorough study of ammonia and a few other liquids has shown chemists that water is not the unique solvent that it was once thought to be.

**Commercial Production of Ammonia.** As pointed out earlier, the most striking chemical property of nitrogen is its inactivity. Shortly before World War I broke out in 1914, the German chemist Fritz Haber invented a process for making ammonia directly from nitrogen and hydrogen.<sup>1</sup> The key to the problem of how nitrogen could be made to react directly with hydrogen lay in finding a catalyst for the reaction. Haber found that iron oxide containing traces of other metal oxides would catalyze the reaction. Although other catalysts have been developed, iron or iron oxide is usually the main ingredient in the modern mixed catalysts.

The equilibrium reaction

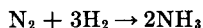


was discussed from several standpoints in Chap. 12.

<sup>1</sup> Some historians have pointed out that the stock pile of Chilean nitrate in Germany in 1914 was not large enough to provide explosives for a long war. When it became evident that the war was not going to be won quickly, the Germans turned to the new Haber process. After months of feverish activity, it was developed to the point where it provided enough ammonia to supply the munitions industry. Thus it is possible that the new ammonia industry enabled the Germans to prolong the war by two or three years.

GROUP VA:  
THE NITROGEN FAMILY

A detailed record of experimentally determined yields of ammonia under various conditions was given in Table 12-1. From that table we see that the amount of ammonia formed at equilibrium is at a maximum when the pressure is high and the temperature is low. On the basis of those data we would pick a temperature of 200°C and a pressure of 1,000 atm as ideal. But those conditions are not as "ideal" as we might expect, because at a temperature of 200°C the reaction



is too slow. To make the reaction occur at a reasonably rapid rate, the temperature must be raised to 500° or more, even though the percentage of ammonia produced is lowered.

A pressure of 1,000 atm requires a heavy investment in pumps and high-pressure equipment. Moreover, the equipment must be made of a special steel alloy, because, at a high temperature and pressure, hydrogen gas will leak through ordinary steel. However, plants have been constructed that operate at pressures near 1,000 atm. In this country, production is generally carried on at pressures of 200 to 350 atm and at temperatures between 500° and 600°C.

A recent design for relatively small ammonia plants, producing 60 to 100 tons/day, is described in Fig. 23-7; several small catalytic vessels, up to 20 ft tall, are used instead of the usual single 60- to 70-ft tower. Small plants are desirable in some localities, because the need for ammonia is so widespread. The most common raw material is natural gas, consisting chiefly of methane,  $\text{CH}_4$ . The gas is reacted

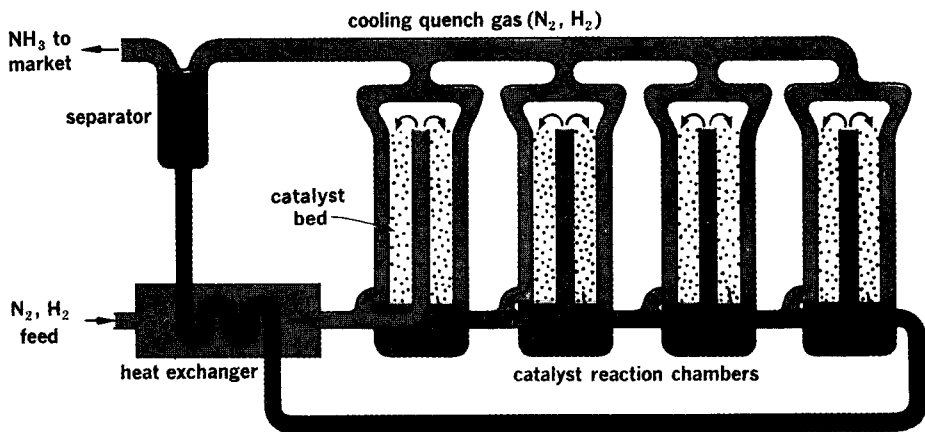


FIG. 23-7

The Haber process. The catalyst beds are indicated by shading; path of unreacted  $\text{N}_2$  and  $\text{H}_2$  is shown by black arrows; and path of  $\text{NH}_3$  is shown by colored arrows. After cooling the outside of a catalyst chamber, the cool quench gas is directed into the main circulating stream. (See *Chemical and Engineering News*, 38 [Dec. 30, 1963].)

with steam and air<sup>1</sup> to produce a  $N_2-H_2-CO_2$  mixture; the carbon dioxide and other impurities are removed, and the resulting 1:3 mixture of nitrogen and hydrogen is fed into the system.

As shown in Fig. 23-7, the  $N_2-H_2$  mixture is first heated to reaction temperature in a heat exchanger and then passed into the catalytic chambers. The catalyst becomes so hot, owing to the exothermic synthesis reaction, that some cool gas must be passed into the catalytic chambers to quench the catalyst to about  $500^\circ C$ . One pass through a bed of catalyst does not convert all the  $N_2-H_2$  mixture to the equilibrium mixture of  $N_2-H_2-NH_3$ , so that the gas is passed successively through three more catalytic chambers. Then the hot  $N_2-H_2-NH_3$  mixture is led into the heat exchanger and cooled by being used to heat the incoming  $N_2-H_2$  feed gas. The cooled  $N_2-H_2-NH_3$  is next pumped to the separator; the  $NH_3$  is put into tanks for shipment, and the  $N_2$  and  $H_2$  are recycled into the system to continue riding the merry-go-round from which they can only jump off as ammonia,  $NH_3$ . As is true of the production of sulfuric acid, the Haber process is continuous and requires few workmen.

Considerable ammonia and ammonium compounds are by-products in the production of coke from coal, but about 88 per cent of our total ammonia production of approximately 8,600,000 tons annually is made by the Haber process. Almost half of this ammonia is converted into ammonium nitrate for use as a fertilizer:



A large amount of ammonia is converted into nitric acid; some is absorbed in water to make aqua ammonia (household ammonia). Liquid ammonia, under a pressure of 8 to 10 atm, is shipped in iron cylinders and in tank cars.

## AMMONIUM COMPOUNDS

The  $NH_4^+$  ion is a perfect tetrahedron in which all the hydrogen atoms are identical; the positive charge is uniformly associated with the whole ion instead of being more on one atom than on another. In its compounds the  $NH_4^+$  ion acts very much like the  $K^+$  and  $Rb^+$  ions, which have the same charge and are of about the same size (radii:  $K^+$ , 1.33Å;  $Rb^+$ , 1.48Å;  $NH_4^+$ , about 1.52Å).

Ammonium compounds as a class are noted for their great solubility in water. Some of the important compounds are listed in Table 23-7.

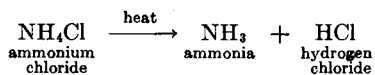
<sup>1</sup> Compare with the steam-hydrocarbon method discussed in Chapter 6.

GROUP VA:  
THE NITROGEN FAMILY

TABLE 23-7 *Ammonium compounds*

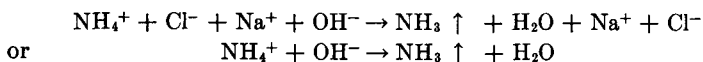
name	formula	uses
ammonium chloride	$\text{NH}_4\text{Cl}$	as a "flux" for cleaning iron before galvanizing and for cleaning metals before soldering; used in dry cells and in preparing fabrics for dying
ammonium fluoride	$\text{NH}_4\text{F}$	for etching glass
ammonium sulfate	$(\text{NH}_4)_2\text{SO}_4$	fertilizer; except for $\text{NH}_3$ , cheapest source of $\text{NH}_4^+$ ions
ammonium sulfide	$(\text{NH}_4)_2\text{S}$	common reagent for qualitative analysis; used in making polysulfides
ammonium carbonate	$(\text{NH}_4)_2\text{CO}_3$	smelling salts
ammonium nitrate	$\text{NH}_4\text{NO}_3$	fertilizer; explosive

Most ammonium compounds are sufficiently stable to exist indefinitely at room temperature, but they decompose when strongly heated;  $\text{NH}_3$  gas is usually one of the products:



The action of heat on a solution of ammonium nitrite,  $\text{NH}_4\text{NO}_2$ , was described earlier in this chapter.

In water solution the ammonium ion reacts with strong bases in this way:



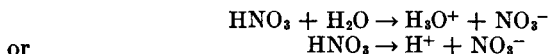
The presence of the  $\text{NH}_4^+$  ion in solution can be demonstrated by adding a strong base, for example, sodium hydroxide, and heating. The ammonia gas that vaporizes from the solution can be detected by its odor or by holding a piece of moist red litmus paper in the fumes (the litmus turns blue).

Ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , commonly used as a fertilizer, has also been used as an explosive in bombs and shells. An intimate mixture of ammonium nitrate and TNT (trinitrotoluene) is almost as powerful as the same weight of pure TNT and is cheaper to use. Although normally very difficult to detonate, ammonium nitrate has been responsible for some disastrous peacetime explosions.

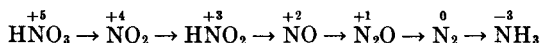
It is interesting that all common explosives are nitrogen-containing compounds. Other examples, in addition to those just mentioned, include nitroglycerin and cellulose nitrate. Such compounds tend to decompose to form nitrogen and other gases in violent exothermic reactions. One solid propellant for rockets is reported to be a mixture of ammonium perchlorate and aluminum held in a plastic mold of nitroglycerine and cellulose nitrate. Fatal explosions have occurred in plants where these propellants are manufactured.

## NITRIC ACID

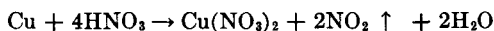
Nitric acid is the water solution of the colorless liquid covalent compound, hydrogen nitrate,  $\text{HNO}_3$ . Hydrogen nitrate dissolves in and reacts with water to form a very strong acid solution:



Along with sulfuric and hydrochloric it is one of the most useful and common acids known. Nitric acid is noted as a strong oxidizing agent. When it reacts in this capacity, nitrogen changes from a +5 oxidation state to a lower one. Because nitrogen can exist in any oxidation state from +5 to -3, the low oxidation state actually attained—that is, the reduction product of nitric acid—depends on several factors, including activity of the reducing agent, concentration of the nitric acid, and temperature. The more common steps can be summarized as follows:



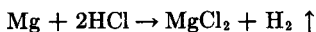
The most common reduction products evolved when nitric acid reacts with a metal are the gases *nitrogen dioxide* and *nitric oxide*. Because  $\text{NO}_2$  is brown and  $\text{NO}$  is colorless, they are easily distinguished.<sup>1</sup> The more concentrated the nitric acid, the greater the tendency for  $\text{NO}_2$  to be formed. Consider copper, a metal that is not attacked by hydrochloric or cold sulfuric acid, because it is not oxidized by hydrogen ions. With concentrated nitric acid the products are  $\text{NO}_2$ ,  $\text{Cu}(\text{NO}_3)_2$ , and  $\text{H}_2\text{O}$ :



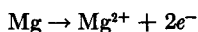
When dilute acid is used, the products are  $\text{NO}$ ,  $\text{Cu}(\text{NO}_3)_2$ , and  $\text{H}_2\text{O}$ :



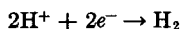
Metals above hydrogen in the activity series are readily oxidized by hydrogen ions. Magnesium reacts with hydrochloric acid as follows:



Oxidation equation:



Reduction equation:



When such a metal reacts with nitric acid, we might expect two reduction products, one from the reduction of hydrogen ions (to

<sup>1</sup> But remember that  $\text{NO}$  reacts with the oxygen in the air to yield  $\text{NO}_2$ .

**GROUP VA:  
THE NITROGEN FAMILY**

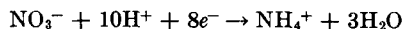
elemental hydrogen) and the other from the reduction of +5 nitrogen (to NO, N<sub>2</sub>O, N<sub>2</sub>, NH<sub>3</sub>, etc.); this is often the case. Usually, however, hydrogen does not make up an appreciable amount of the final reduction products. Rather, they are largely those which arise from the reduction of the +5 nitrogen. With dilute nitric acid and with active metals, such as magnesium and zinc, it is possible for the reduction of +5 nitrogen to proceed to the formation of ammonia (-3 nitrogen). The ammonia (a base) then reacts with excess nitric acid to form the salt ammonium nitrate, NH<sub>4</sub>NO<sub>3</sub>:



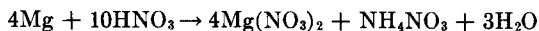
Oxidation equation:



Reduction equation:



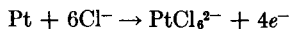
Balanced overall equation:



It must be understood that writing NO<sub>3</sub><sup>-</sup> as the oxidizing agent in nitric acid is a simplification. Solutions of such salts as potassium nitrate, KNO<sub>3</sub>, calcium nitrate, Ca(NO<sub>3</sub>)<sub>2</sub>, and iron(II) nitrate, Fe(NO<sub>3</sub>)<sub>2</sub>, have nitrate ions in them, but they are not as strong oxidizing agents as nitric acid solutions, in which the NO<sub>3</sub><sup>-</sup> and H<sup>+</sup> ions are both present.

*Aqua regia*, a mixture of concentrated nitric acid (1 volume) and concentrated hydrochloric acid (3 volumes), is often more effective in dissolving metals and minerals than nitric acid alone. The mixture dissolves gold and platinum, whereas neither of the acids will do so when used separately. The efficiency of this mixture of acids is thought to depend on (1) the strong oxidizing action of nitric acid and (2) the tendency of chloride ions to form stable complex ions, as mentioned in Chap. 19. For platinum the equations are:

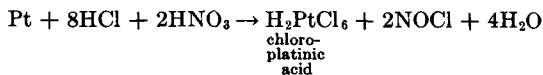
Oxidation:



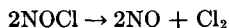
Reduction:



Overall:

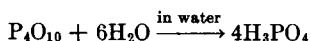


*Nitrosyl chloride*, the product of the reaction of nitric acid with hydrochloric acid, decomposes rapidly when heated:

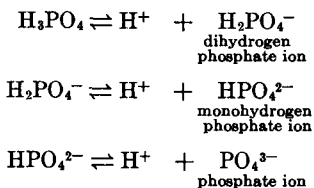


## PHOSPHORIC ACID

Phosphoric acid is the water solution of hydrogen phosphate,  $\text{H}_3\text{PO}_4$ . The anhydrous compound (a viscous, colorless liquid at room temperature) is seldom prepared. The acid solution of any concentration can be made easily by dissolving phosphoric oxide,  $\text{P}_4\text{O}_{10}$ , in water:

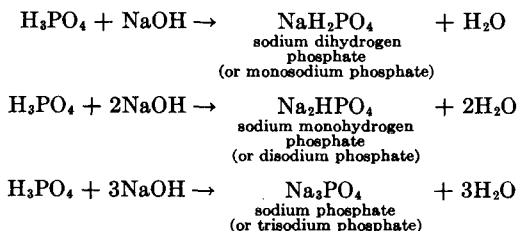


This weak triprotic acid ionizes in the following steps:



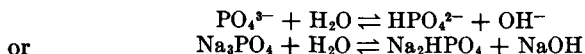
In a solution of moderate concentration most of the compound is present as  $\text{H}_3\text{PO}_4$  molecules. There are also moderate amounts of  $\text{H}^+$  and  $\text{H}_2\text{PO}_4^-$  ions, a small concentration of  $\text{HPO}_4^{2-}$  ions, and a very minute amount of simple  $\text{PO}_4^{3-}$  ions.

If a base is added to the acid solution, the following reactions will take place, depending on the amount added:



Salts of phosphoric acid are also known with two cations other than hydrogen. An example is magnesium ammonium phosphate,  $\text{MgNH}_4\text{PO}_4$ .

Soluble phosphates hydrolyze in water to make basic solutions, because the phosphate ion has sufficient proton affinity to take a hydrogen ion away from water:



For this reason, solutions of the soluble phosphates lower the surface tension of water and have a "soapy feel" like sodium hydroxide or potassium hydroxide solutions. Trisodium phosphate is used as an additive in many soap and detergent powders.

Some well-known compounds of the nitrogen family are described in Table 23-8.



**GROUP VA:  
THE NITROGEN FAMILY**

**TABLE 23-8**     *Compounds of group VA elements*

formula	chemical name (common name)	remarks
$\text{KNO}_3$	potassium nitrate (saltpeter)	mixed with sulfur and charcoal to make black powder
$\text{Na}_3\text{PO}_4$	trisodium phosphate	water softener; added to many powdered soaps and detergents
$\text{Ca}(\text{H}_2\text{PO}_4)_2$	monocalcium phosphate	produced by action of sulfuric acid on phosphate rock; resulting mixture of monocalcium phosphate and calcium sulfate called superphosphate fertilizer
$(\text{NH}_4)_2\text{HPO}_4$	diammonium phosphate	fertilizer with both N and P in one compound
$\text{As}_2\text{O}_3$	arsenious oxide (common name is arsenic)	active ingredient in insecticides, weed killers; fatal human dose, about 0.1 g
$\text{P}_4\text{O}_{10}$	phosphoric oxide (called phosphorus pentoxide because of old formula, $\text{P}_2\text{O}_5$ )	has greater affinity for water than any other common substance, even $\text{H}_2\text{SO}_4$ ; used to dry gases
$\text{N}_2\text{O}$	nitrous oxide (laughing gas)	mild anesthetic; patient often has such vivid dreams that he mistakes them for reality

**CHAPTER REVIEW**

*Topics*

Properties of the nitrogen family, nitrogen fixation, nitrogen cycle, oxidation states, acidic or basic character of hydroxides, production of the elements, ammonia chemistry, Haber process, nitric acid chemistry, phosphoric acid.

*Exercises*

1. By a consideration of specific properties, cite evidence to support the statement that the change from nonmetallic to metallic character is quite clear in group VA.
2. Can their solubilities in carbon disulfide be correlated with the molecular structures of white and red phosphorus; with their melting points?
3. Which would you consider to have the larger molecules, a perfect crystal of white phosphorus,  $\text{P}_4$ , or a perfect crystal of antimony, Sb?
4. *a.* Although group VA is called the nitrogen family, nitrogen itself is somewhat apart from the group in properties. Cite some examples.  
*b.* Is this relation of nitrogen to its group unusual, or are there similar instances in other groups?
5. Although elemental nitrogen has a higher electronegativity than phosphorus, the latter is much more active chemically. Explain.
6. Describe three nitrogen-fixation processes. Tell if they are natural or artificial.

7. What is a nitride? Describe how you might prepare the nitride of magnesium. Write the equation for the reaction.
8. a. By means of equations, show how NO could be produced in the atmosphere by a chain reaction initiated by lightning.  
b. Show, with equations, why the chain reaction would not long continue to produce NO.
9. The formula for sulfur monochloride is  $S_2Cl_2$ . Why would such a poor name ever be chosen for the compound?
10. What is the oxidation state of the nitrogen family element in the following compounds:  $P_2O_3$ ,  $As_2O_5$ ,  $NaNO_2$ ,  $SbH_3$ ,  $BiCl_3$ ,  $(NH_4)_2SO_4$ ?
11. Complete the following equations:
 

$P_4 + O_2 \rightarrow$	$As_2O_3 + H_2O \rightarrow$
$As_4 + Cl_2 \rightarrow$	$PCl_3 + H_2O \rightarrow$
$SbCl_3 + H_2O \rightarrow$	$H_3AsO_4 + NaOH \rightarrow$
12. Write a hypothetical equation for the decomposition of stibine and explain why the decomposition might be explosive.
13. Bismuth triiodide hydrolyzes more readily than the trichloride. Why might this be? Write an equation for the hydrolysis of the triiodide.
14. a. Arsenious acid,  $HAsO_2$ , is amphoteric. Write ionic equations to show how it would react in acidic or in basic solutions.  
b. Repeat the above for aluminium hydroxide,  $Al(OH)_3$
15. Outline the chemical steps in the production of elemental phosphorus.
16. What is the commercial source of elemental nitrogen? Explain how fairly pure nitrogen is obtained from it.
17. Write the equation for the reaction that occurs when a water solution of ammonium nitrite is warmed. Do chemical storerooms stock ammonium nitrite? Why or why not?
18. From the shape of the ammonia molecule, what type of hybrid orbitals would be predicted for it? Diagram hybrid orbital structures for ammonia and ammonium ion using the style in Table 19-9.
19. How well do ammonia and water obey Trouton's rule? (See also Exercise 47, Chap. 16, and Exercise 28, Chap. 21.)
20. Nitrous acid and phosphorous acid are well known, but not "bismuthous" acid. Account for this on the basis of atomic theory.
21. Are the oxides of the nitrogen family reduced by hot carbon? Does this chemical property have any commercial importance? Explain.
22. By means of diagrams explain how the ammonia molecule can have a dipole moment in spite of its motion of inversion. Also explain why it is thought that the dipole moment of such a molecule would be zero if the rate of inversion were rapid enough.

**GROUP VA:**  
**THE NITROGEN FAMILY**

23. Write equations for reactions in the nitrogen system that are analogous to the following water-system reactions:
- $\text{Mg(OH)}_2 \xrightarrow{\text{heat}} \text{MgO} + \text{H}_2\text{O}$
  - $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} + 6\text{NH}_3 \rightarrow \text{CaCl}_2 \cdot 6\text{NH}_3 + 6\text{H}_2\text{O}$
  - $2\text{HNO}_3 + \text{Zn(OH)}_2 \rightarrow \text{Zn(NO}_3)_2 + 2\text{H}_2\text{O}$
  - $2\text{NaOH} + \text{Zn(OH)}_2 \rightarrow \text{Zn(ONa)}_2 + 2\text{H}_2\text{O}$
24. Is the reaction of ammonia with oxygen to yield nitrogen and gaseous water exo- or endothermic? Calculate  $\Delta H_f^\circ$ .
25. Explain why the catalyst chambers in an ammonia-synthesis plant tend to become overheated, and why the temperature must be kept from going, say,  $200^\circ$  higher than the desired temperature.
26. a. Write reactions to show how methane, air, and steam could react to give a mixture of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{CO}_2$ .  
b. How could the carbon dioxide be separated from the mixture in (a) leaving the nitrogen and hydrogen?
27. a. Consider Fig. 23-7. Could a sample of  $100 \text{ ft}^3$  of a 1:3 mixture of nitrogen and hydrogen be completely changed into ammonia with such apparatus. Explain fully.  
b. If the change were possible, what volume of ammonia would be obtained?
28. Pure ammonia is shipped commercially as a liquid, but hydrogen is shipped as a gas. Why?
29. Ammonium nitrate, although difficult to detonate, is an explosive compound, associated with some of the most disastrous peacetime explosions in history. Write a hypothetical equation for the decomposition reaction and suggest an explanation for its exothermic character.
30. Phosphate rock is not suitable as such as a plant food because of its insolubility in water. One method for overcoming this difficulty is to treat the pulverized rock with sufficient sulfuric acid to convert the insoluble tricalcium phosphate into the soluble monocalcium phosphate. Write the equation for the reaction.
31. a. Write a balanced equation for the violently exothermic reaction between ammonium perchlorate and aluminium, assuming the products are aluminium oxide, nitrogen, water, and chlorine.  
b. What are two reasons why this mixture might be suitable as a solid propellant for rockets?
32. When copper reacts with dilute nitric acid in a test tube, the gas formed immediately in the test tube is colorless, but a brownish gas issues from the mouth of the tube. Explain with equations.
33. By careful thermal decomposition of ammonium nitrate, at about  $200^\circ\text{C}$ , nitrous oxide can be formed. Write a hypothetical equation for the reaction.
34. With concentrated nitric acid copper reacts to produce (as one of the products)  $\text{NO}_2$ , with dilute acid to produce  $\text{NO}$ . Write oxidation and reduction ionic equations for both these cases.

35. a. Use a general electronic formula such as  $\text{H}:\ddot{\text{O}}:\ddot{\text{E}}::\ddot{\text{O}}:$  to account for amphotericism.  
 b. On the basis of the above general formula, account for the fact that when E is nitrogen the compound has a pronounced acid character, when E is bismuth the compound acts as a base, and when E is antimony or arsenic the compound is amphoteric.
36. Draw proposed electron dot formulas for  $\text{HNO}_2$  and  $\text{HNO}_3$ . Explain why the former is a much weaker acid than the latter.
37. Write the oxidation, reduction, and overall balanced equations for the action of aqua regia on gold. The  $\text{AuCl}_4^-$  ion is one of the products.
38. Write a hypothetical equation for a metal M, with an ion  $\text{M}^{3+}$ , which reacts with nitric acid to yield elemental nitrogen as the reduction product. Also, write the ionic equations for the oxidation and reduction reactions.
39. Write equations for the following reactions:
  - a. Lithium and nitrogen
  - b. Combustion of bismuth
  - c. Combustion of phosphine
  - d. Production of arsenic from realgar
  - e. Roasting in air of arsenical pyrites
  - f. Lime and household ammonia (can be violent)
  - g. Nitric acid and household ammonia (can be violent)
  - h. Zinc and nitric acid
  - i. Lead and nitric acid (yields NO)
  - j. Silver and hot, concentrated nitric acid (yields  $\text{NO}_2$ )
  - k. Explosion of nitrogen trichloride,  $\text{NCl}_3$
40. Show how the reaction of ammonium sulfate and potassium amide in liquid ammonia could be considered an acid-base reaction.
41. Often we read that there may or may not be life on a certain other planet because it does or does not have water in its atmosphere. However, some planets have ammonia-rich atmospheres. Is there any basis for thinking than an ammonia environment could support life of some sort as our water environment does?
42. What volume of 0.199 N KOH would be required to convert 50.0 ml of 0.333 N  $\text{H}_3\text{PO}_4$  to tripotassium phosphate?
43. About how many cubic feet of air at  $20^\circ\text{C}$  and 740 mm will be required to supply the nitrogen to make a ton of ammonia?
44. What should be the main products resulting from the "burning" of black powder? Note that atmospheric oxygen is not involved.
45. Solutions of household ammonia or trisodium phosphate are commonly used in cleaning. Write ionic equations for each to show that there is one ion common to the two solutions.

**GROUP VA:**  
**THE NITROGEN FAMILY**

46. What products would you expect to prepare by adding together solutions containing the following, then evaporating, and baking to dryness? Calculate the weight of each compound product:
- a. 10 g  $\text{H}_3\text{PO}_4$  and 5 g NaOH      c. 10 g  $\text{H}_3\text{PO}_4$  and 15 g NaOH  
b. 10 g  $\text{H}_3\text{PO}_4$  and 10 g NaOH
47. Explain why it is theoretically desirable to carry out the Haber process at high pressure and low temperature. Then explain why moderate pressure and moderate temperature are actually used.

**SUPPLEMENTARY READING**

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## CARBON, SILICON,

## AND BORON



We have studied three nonmetal families of the periodic table in detail—groups VA, VIA, and VIIA. Of these, the halogens are most like one another. There is a great difference in electron affinity between fluorine and iodine, but all the group VIIA elements are nonmetals. In the next group, the trend from oxygen to polonium goes from nonmetals to a metalloid element. In group VA the change is even greater—from the nonmetals nitrogen and phosphorus, through the metalloid elements arsenic and antimony, to the metallic bismuth.

In group IVA we find that the elements carbon, C, and silicon, Si, differ so much from the other family members—germanium, Ge, tin, Sn, and lead, Pb—that it is not satisfactory to study the five elements collectively. In fact, the metallic elements in group IVA (Ge, Sn, and Pb) resemble the elements in group IVB (Ti, Zr, and Hf) more than they resemble the nonmetallic carbon and silicon. There is a greater similarity between the A and B families in group IV than in any other group. The trends in the A families are summarized below:

IVA	VA	VIA	VIIA
nonmetal	nonmetal	nonmetal	nonmetal
↓	↓	↓	↓
metal	metalloid		
↓	↓	↓	↓
metal	metal	metalloid	nonmetal

In this chapter we shall take up the three nonmetals yet to be discussed—carbon and silicon from group IVA and boron from group IIIA. Boron is so like silicon that it is a good example of an element that resembles an element in another family more closely than those in its own family.

## PROPERTIES OF CARBON, SILICON, AND BORON

### PHYSICAL PROPERTIES

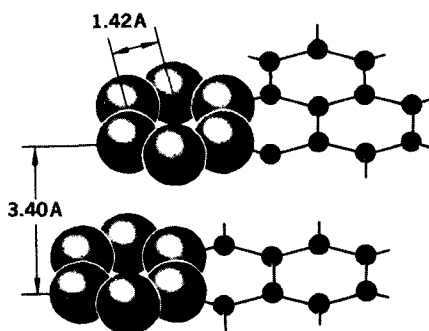
The very high melting and boiling points of boron, carbon, and silicon distinguish them from the other nonmetals (see Table 24-1).

TABLE 24-1 *Physical properties of boron, carbon, and silicon*

	boron B	carbon C	silicon Si
melting point, °C	2040		1410
boiling point, °C	2550 (sublimes)	4347 (sublimes)	2677
electron distribution	2,3	2,4	2,8,4
ionization energy, ev	8.3 (190 kcal)	11.2 (260 kcal)	8.1 (190 kcal)
covalent radius, A	0.80	0.77	1.17
crystal radius, A	0.2 (B <sup>3+</sup> )	0.15 (C <sup>4+</sup> )	0.41 (Si <sup>4+</sup> )
electronegativity	2.0	2.5	1.8

All three are rigid solids that may be thought of as giant molecules consisting of a huge number of atoms. Both boron and silicon can be made in only one crystalline form, whereas carbon occurs in two well-defined crystalline forms. All three elements can be obtained in one or more amorphous modifications. The common amorphous forms of carbon are charcoal, coke, carbon black, and boneblack.<sup>1</sup>

The crystalline forms of carbon are famous for their physical differences. One, *graphite*, is a soft black substance that actually feels greasy; as a dry powder it is used as a lubricant, especially for locks. The other, *diamond*, a colorless solid capable of being cut into brilliant crystals, is the hardest, most abrasive mineral known. Yet both these substances consist of only carbon atoms.



In graphite, carbon atoms crystallize in layers with hexagonal symmetry. The atoms are much closer to their neighbors in the same layer than to atoms in an adjacent layer.

FIG. 24-1

In the case of graphite, the atoms crystallize in a pattern of layers that slide over one another easily (Fig. 24-1). In contrast, the carbon

<sup>1</sup> Although these forms are often described as amorphous, recent work has shown that some of them are microcrystalline (graphite structure).

The diamond structure. Carbon atoms crystallize with tetragonal symmetry, since each atom has four nearest neighbors.

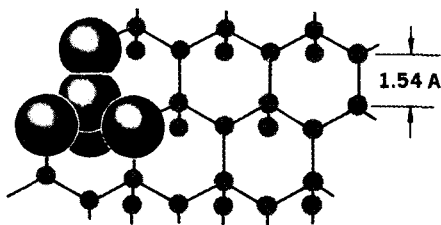


FIG. 24-2

atoms in the diamond structure have strong bonds with neighbors in three dimensions, each atom being bound by equally strong covalent bonds to atoms on all sides (Fig. 24-2).

Boron and silicon have ionization energies and electronegativities that mark them as borderline elements, but the higher values for carbon show it to be a true nonmetal.

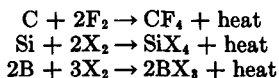
All three elements are relatively poor conductors of heat and electricity, although the graphite form of carbon conducts electricity better than most other nonmetals.<sup>1</sup> Because it adheres well to many materials and is a conductor, graphite is often brushed over nonconducting surfaces, such as leather or plastic, that are to be electroplated.

The atoms of boron, carbon, and silicon are very small compared with other atoms. The ordinary crystal radii of these elements are even smaller, because the atoms are usually in positive oxidation states.

## CHEMICAL PROPERTIES

All three elements are quite unreactive at ordinary temperatures, especially as large crystals. When they do react, there is no tendency for their atoms to lose outer electrons and form simple cations, such as  $B^{3+}$ ,  $C^{4+}$ , and  $Si^{4+}$ . Small ions of this type would have such high charge densities that their existence is unlikely. Instead, the atoms usually react by sharing electrons to form covalent bonds.

**Reactions with Halogens.** Silicon and boron react with the halogens, even burning in gaseous fluorine. Carbon reacts directly with fluorine (X refers to a halogen atom):

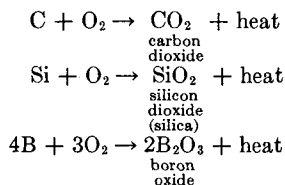


<sup>1</sup> In the diamond structure the electron pairs are held so strongly that electrical conductivity is very low. In the graphite structure the electrons in the bonds between the layers are not held so tightly and hence are free to move through the crystal and conduct electricity.

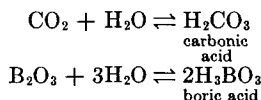


**CARBON, SILICON,  
AND BORON**

**Common Oxy-acids.** When heated in air, these elements react with the oxygen in highly exothermic combustion reactions:

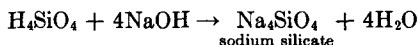


All three of these oxides are *acidic*. Two of them react with water to give very weak acid solutions:



Silicic acid,  $\text{H}_4\text{SiO}_4$ , also well known, is not formed in appreciable concentration by the direct union of  $\text{SiO}_2$  and  $\text{H}_2\text{O}$ .

The acidity of a silicic acid solution is hardly measurable because of the extremely low solubility of the acid. However, the solid acid reacts with a base:

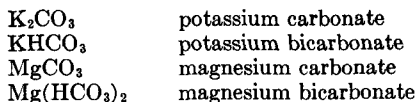


When partially dried, silicic acid is called silica gel (a material that looks something like rock salt). In this form it has great adsorbent capacity for vapors of water, sulfur dioxide, nitric acid, benzene, and other substances. It is widely used as a dehumidifier.

Boric acid has been a stand-by in the family medicine chest for years. Available at drugstores in the form of small, glittering, colorless platelets, it dissolves readily in water, yielding a mild antiseptic solution.

None of the three acids is of great use commercially as an acid, with the possible exception of carbonic acid; this gives carbonated drinks their slightly sour taste and effervescence.

**Salts of Oxy-acids.** The salts of the acids above are well known. Carbonic acid, as a typical diprotic acid, reacts with bases to give such carbonates and bicarbonates as



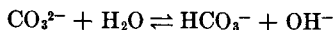
Two simple silicic acids are orthosilicic acid,  $\text{H}_4\text{SiO}_4$ , and meta-silicic acid,  $\text{H}_2\text{SiO}_3$ . Salts of these two acids include

$\text{Na}_2\text{SiO}_3$	sodium metasilicate
$\text{Na}_4\text{SiO}_4$	sodium orthosilicate
$\text{Mg}_2\text{SiO}_4$	magnesium orthosilicate
$\text{LiAl}(\text{SiO}_3)_2$	lithium aluminum metasilicate

All the silicates except those of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ , and  $\text{NH}_4^+$  are practically insoluble in water.

A great many simple and complex borates are known; but aside from borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , they are not of sufficient general interest to be mentioned here.

All the soluble carbonates, silicates, and borates form basic solutions when dissolved in water. The  $\text{CO}_3^{2-}$ ,  $\text{SiO}_3^{2-}$ , and  $\text{BO}_3^{3-}$  ions act as bases to remove protons from water (hydrolysis; see Chap. 13):



A solution of sodium carbonate or sodium silicate or sodium borate turns red litmus blue because of the formation of  $\text{OH}^-$  ions by reactions similar to the one above.

**Formation of Large Molecules.** A most important chemical property of carbon, silicon, and boron is their tendency to form huge molecules. We should note two differences between silicon and boron on the one hand, and carbon on the other. The first is that carbon atoms join with one another to form a limitless variety of chains or rings of atoms. The second is that carbon atoms tend to form single, double, and triple covalent bonds, whereas silicon and boron tend to form only single bonds (four and three single bonds, respectively). Beginning with Chap. 25, several chapters are devoted to the subject of carbon compounds.

The linking of  $(\text{SiO}_4)$  tetrahedra in one form of silica,  $\text{SiO}_2$ .

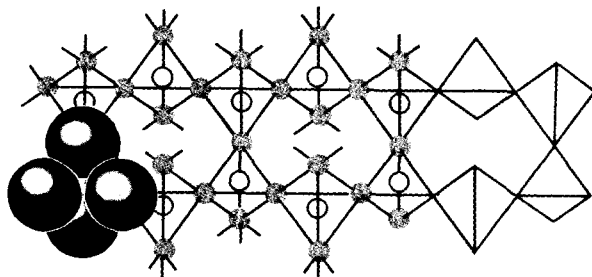
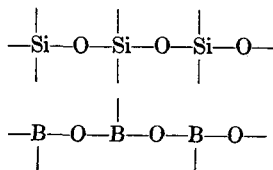


FIG. 24-3

Silicon and boron form giant molecules and ions in which oxygen atoms occupy alternate positions. These structures are built up in this fashion:



Silicon-containing and boron-containing rocks and minerals are commonly high-melting, hard, brittle solids, each piece of which is a continuous lattice of tightly bound atoms. An example of such a solid is silicon dioxide, which occurs in nature in the form of quartz, agate, sand, etc. One  $\text{SiO}_2$  crystal structure is shown in Fig. 24-3.

## **OCCURRENCE, PREPARATION, AND USES**

### **CARBON**

Carbon occurs in the earth's crust in both the free and combined states. The most common material that contains elemental carbon is anthracite coal; however, there is also combined carbon in it. Bituminous or soft coal contains some elemental carbon, but it is largely a mixture of complex and ill-defined carbon compounds. Both of the crystalline forms of carbon are found in nature; graphite is found in considerable quantities in deposits in Siberia, Ceylon, Canada, and the United States.

The principal natural compounds of carbon are the organic substances formed in the tissues of living things, both plant and animal, and in materials derived from living things, such as coal and petroleum. Among the common inorganic carbon compounds are carbon dioxide and the carbonate rocks, particularly calcium carbonate,  $\text{CaCO}_3$ . Carbonates of other group IIA elements are well known as minerals: magnesium, strontium, and barium carbonates— $\text{MgCO}_3$ ,  $\text{SrCO}_3$ , and  $\text{BaCO}_3$ , respectively.

Elemental carbon has many uses. *Graphite*, either natural or man-made, is used as the black constituent in ordinary pencil leads, as the pigment in black paints, in the manufacture of crucibles and electrodes to be used at extremely high temperatures, and as a dry lubricant.

Both of the polymorphic forms of carbon vaporize when heated to about  $3500^\circ\text{C}$ . On cooling slightly, the vapors condense in the form of graphite. This is the process for the commercial production of graphite from anthracite coal and from coke (see Fig. 24-4). Coarsely ground carbon is piled in a container made of heat-resistant material. A little iron oxide is included as a catalyst. A core of special carbon conducts the high-voltage current and is thereby heated to a very high temperature. At this temperature the coarsely ground carbon is changed into graphite. A layer of carbon and sand insulates the furnace and keeps air out. Diamonds could be converted into graphite by this process, a project in which there is little interest.

*Diamonds*, particularly discolored and small ones, are used in industry for making the hardest abrasive powders, for grinding wheels and the tips of drills and saws. Culminating 125 years of world-wide experimentation, application by General Electric scientists in 1954 of thermodynamic theories led to the commercial production of man-

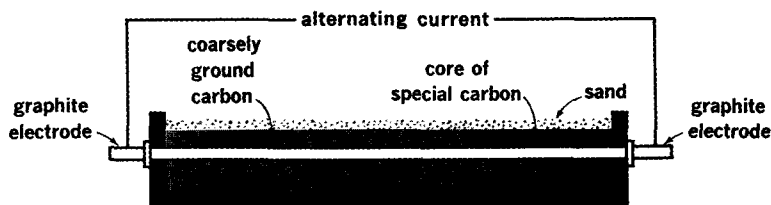


FIG. 24-4

The Acheson furnace for producing graphite.

made diamonds. Pressures greater than 1,500,000 psi and temperatures above 2700°C were required. Man-made diamonds are not so large or so brilliantly white as the fine stones found in nature, but in most other characteristics they are identical with natural diamonds.

*Carbon black*, the sooty product formed when natural gas is incompletely burned, is mainly carbon. Light and fluffy, its extremely small particles are used in printing inks, carbon paper, shoe polish, and paint. When mixed with rubber, it increases the elasticity and durability of rubber so necessary in automobile tires. From 600 to 950 lb of carbon black is required per ton of rubber in tires. Carbon black is made by burning natural gas in a limited amount of air or by the thermal decomposition of natural gas. In the channel process, the smoky flame is directed against a water-cooled rotating iron cylinder, and the carbon that collects is scraped off. In the furnace process, the carbon resulting from an incomplete combustion is separated from the combustion gases in Cottrell precipitators.

*Boneblack* is made by the destructive distillation<sup>1</sup> of bones. It is composed chiefly of calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , its active ingredient being finely divided carbon that has a great adsorptive capacity. It can be used in filters to adsorb coloring matter (for example, to decolorize crude sugar or molasses) and in gas masks to remove molecules of poisonous gases from the air.

*Charcoal* and *coke* are made by the destructive distillation of wood and coal,<sup>2</sup> respectively. Both charcoal and coke are used as high-quality solid fuels; also charcoal can be made more useful by "activating" by means of special treatment (see Chap. 11). Activated charcoal has a greatly increased adsorptive capacity and can be used for the same purposes as boneblack.

## SILICON AND BORON

In spite of their relative inactivity chemically, silicon and boron are not found free in nature. They occur only in oxy-compounds, such as silica, silicates, and borates. The principal boron compounds—

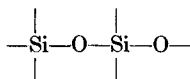
<sup>1</sup> Destructive distillation refers to the process wherein a material is heated out of contact with air. As decomposition takes place, volatile products are boiled off, condensed, and collected. Nonvolatile products are left behind as a residue.

<sup>2</sup> Destructive distillation of these two materials produces valuable products other than charcoal and coke. See methyl alcohol in Chap. 27 and coal tar in Chap. 25 for lists of these products.

# CARBON, SILICON, AND BORON

and they are not abundant—are boric acid,  $\text{H}_3\text{BO}_3$ , and hydrated sodium borate (borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ).

The silicon-oxygen compounds are the most abundant of all the compounds in the earth's crust. Most rocks and minerals<sup>1</sup> are silicates with an



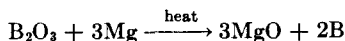
lattice. This lattice can be thought of as derived from  $\text{SiO}_2$  but with atoms of other elements sometimes attached to the silicon and oxygen atoms, sometimes substituted for these atoms. The formulas and names of some of the more abundant groups of minerals containing silicon are listed in Table 24-2.

TABLE 24-2 *Abundant silicon-containing minerals*

mineral group	percentage of minerals in earth's crust	characteristic structure	representative formulas and common names
feldspars	49	crystal large in three dimensions (boxlike)	$\text{KAlSi}_3\text{O}_8$ , orthoclase $\text{NaAlSi}_3\text{O}_8$ , albite $\text{CaAl}_2\text{Si}_2\text{O}_8$ , anorthite $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$ , sodalite
quartz	21	same as above	$\text{SiO}_2$ , silica
amphiboles, or pyroxenes	15	crystal large in one dimension (chainlike)	$\text{CaSiO}_3$ , wollastonite $\text{NaAlSi}_2\text{O}_6$ , jadeite $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ , tremolite (an asbestos)
mica	8	crystal large in two dimensions (layerlike)	$\text{KAl}_2\text{Si}_2\text{AlO}_{10}(\text{OH})_2$ , muscovite $\text{K}_2\text{Li}_3\text{Al}_4\text{Si}_7\text{O}_{21}(\text{OH},\text{F})_3$ , lepidolite

NOTE: The minerals listed here include only silica and the main silicates; yet they account for 93 per cent of the total minerals in the earth's crust. The other 7 per cent is comprised of some of the minor silicates and the myriad non-silicon-containing minerals, such as the carbonates, sulfates, sulfides, oxides.

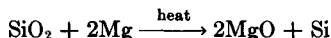
Elemental boron can be prepared as a brown powder by the reduction of boron oxide,  $\text{B}_2\text{O}_3$ , with magnesium or aluminum:



Pure crystalline boron is black, approaches diamond in hardness, but has few uses.

<sup>1</sup> The term *mineral* is restricted to naturally occurring, relatively homogeneous inorganic material with characteristic properties and a composition that is within certain limits. *Rocks* may be made of one or more minerals and may be homogeneous or heterogeneous.

Elemental silicon can be prepared from silica by the same method shown for boron, that is,

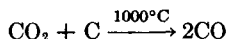


In its crystalline form silicon is gray or black. It has had few uses; however, it is being used as a component in transistors and in certain of the new solar batteries.

## IMPORTANT INORGANIC COMPOUNDS

### COMPOUNDS OF CARBON

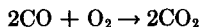
**Carbon Monoxide.** When carbon-containing fuels (for example, wood, coal, gasoline) are burned in the presence of a great deal of air, practically all the carbon combines with oxygen to make carbon dioxide,  $\text{CO}_2$ , but a very little *carbon monoxide*,  $\text{CO}$ , is formed. It is present in small amounts in the fumes from practically all fires. The less air (or oxygen) there is available, the greater the relative amount of carbon monoxide formed. Also, at higher temperatures carbon dioxide tends to react with hot carbon:



Extremely poisonous, carbon monoxide is especially dangerous, because it is colorless and odorless. Even 1 part of the gas in 2,000 parts of air causes death in about four hours.

Carbon monoxide forms a compound with the iron in the hemoglobin molecule in the blood. Normally, oxygen is removed from the air in the lungs by chemical combination with the hemoglobin in the red blood cells. The oxy-hemoglobin, a bright red compound, is then carried through the arteries to the cells, where the oxygen is released to food substances that are in the process of being oxidized to carbon dioxide, water, and other products. The hemoglobin is then carried through the veins back to the lungs, where it again combines with oxygen. This cycle is broken by the presence of carbon monoxide, because the  $\text{CO}$ -hemoglobin bond is stronger than the  $\text{O}_2$ -hemoglobin bond.  $\text{CO}$ -hemoglobin therefore accumulates in the blood stream and prevents the oxy-hemoglobin from carrying on its normal function.

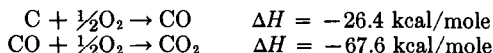
In garages and long tunnels the amount of carbon monoxide may become dangerously high. A patented device, designed to be attached to the exhaust pipes of cars, contains a catalyst for the reaction:



Commercially, carbon monoxide has a number of uses. Mixtures of gases containing it have long been used as fuels; actually, more heat is

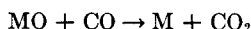
**CARBON, SILICON,  
AND BORON**

liberated when carbon monoxide burns to carbon dioxide than when carbon burns to carbon monoxide:



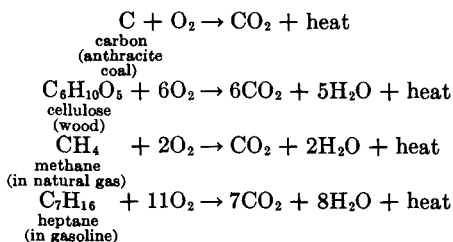
Four important fuel gases are listed in Table 24-3. Of these, only natural gas contains no significant amount of carbon monoxide.

Carbon monoxide reduces many metal oxides to their elements:



This reaction was mentioned in Chap. 20.

**Carbon Dioxide.** Carbon dioxide is the common product of the combustion of carbon-containing fuels:



Carbon dioxide is likewise a component of the breath exhaled by animals, because it results from the oxidation of food in the body. Present in the atmosphere to the extent of about 0.03 per cent, its concentration may rise to 1 per cent in a crowded room.

**TABLE 24-3**     *Fuel gases*

name	composition, per cent		source	approximate heat value, Btu/ft <sup>3</sup> *
water gas	CO	40-50	reaction of steam with hot coal: $\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	300
	H <sub>2</sub>	45-50		
	CO <sub>2</sub>	3-7		
	N <sub>2</sub>	4-5		
producer gas	CO	20-35	coal burned in air and steam under conditions that pro- duce mainly carbon monox- ide and hydrogen	130
	H <sub>2</sub>	5-10		
	N <sub>2</sub>	55-65		
coal gas	H <sub>2</sub>	45-54	by-product in manufacture of coke by destructive distilla- tion of coal	600
	CH <sub>4</sub>	28-34		
	CO	6-7		
natural gas	CH <sub>4</sub>	50-92	gas and oil wells	1000
	C <sub>2</sub> H <sub>6</sub>	2-14		

\*One Btu (British thermal unit) = 252 cal.

Carbon dioxide is not poisonous, but too high a concentration in the air (10 to 20 per cent) is unhealthy, because it lowers the oxygen concentration and has harmful physiological effects (unconsciousness, failure of certain respiratory muscles, and a change in the pH of the blood).

There can also be too little carbon dioxide in a person's system. Fear or excitement may make him breathe so rapidly that carbon dioxide is removed from his blood faster than his cells can replenish it. Convulsions or loss of consciousness results if the acidity of the blood is sufficiently altered. The patient may be revived by having a paper bag put over his head. (A triumph of medical science via Dalton's and Henry's laws: As one breathes the same air over and over, the partial pressure of carbon dioxide increases, thereby increasing the amount dissolved in the blood.)

Large amounts of the gas are found in the water of some geysers and mineral springs. The atmosphere in a cave or valley where carbon dioxide seeps out of fissures in the ground may be dangerous. Because the gas has such high density (44 g/mole compared to 29 g/mole for air), it tends to stay in low places. It can be poured from one vessel to another like a liquid; it even remains in an open beaker for a short time before it diffuses out into the air.

Constantly entering the atmosphere in a variety of ways, carbon dioxide is constantly removed by photosynthesis in plants, the formation of carbonate rocks, and the formation of the shells of marine animals. (See Fig. 30-6.)

The most useful properties of carbon dioxide are described below.

The solid sublimates at  $-78.5^{\circ}$  under a pressure of 1 atm. Solid carbon dioxide is called dry ice because it vaporizes without first melting. It is a convenient, clean refrigerant, especially useful when subzero temperatures are necessary. Crushed solid carbon dioxide in a Dewar flask of alcohol or acetone makes an excellent cold bath for laboratory work (see Fig. 24-5).

It reacts with water to make a dilute solution of carbonic acid,  $\text{H}_2\text{CO}_3$ . Carbonated water—water saturated with carbon dioxide at 3 or 4 atm pressure—is the foundation of our huge soda-water bever-

A low-temperature bath of alcohol cooled with solid carbon dioxide. The sealed glass tube A contains solid ammonia which freezes at  $-77.7^{\circ}\text{C}$ . Tube B contains liquid propane which condenses at  $-42.7^{\circ}$  but freezes at  $-190^{\circ}\text{C}$ .

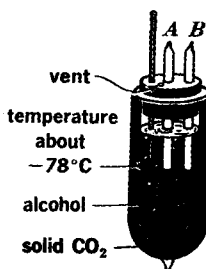


FIG. 24-5



# CARBON, SILICON, AND BORON

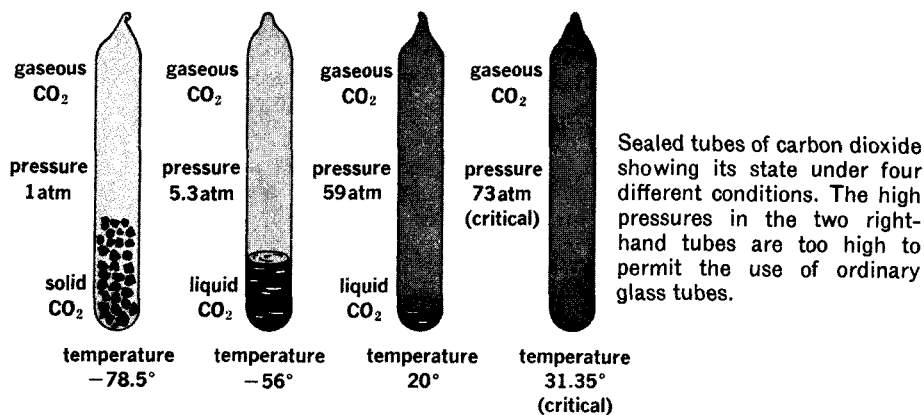


FIG. 24-6

age industry. Removing the cap from a bottle of a carbonated drink releases the pressure, and some of the dissolved gas *effervesces*, or leaves the solution in the form of tiny bubbles (Fig. 13-1). The solubility of carbon dioxide in water follows Henry's law up to about 5 atm pressure (Chap. 10).

Carbon dioxide does not support combustion. Cylinders of gaseous or liquid carbon dioxide under about 60 atm pressure are used as fire extinguishers. A nozzle attached to the cylinder delivers a stream of the gas or liquid that cools itself by expansion. (A little of it is cooled enough to freeze into tiny crystals, producing a cloud of "snow.") Because the gas is so dense, it settles around the base of a fire and smothers it.

The change of state of carbon dioxide with temperature is shown in Fig. 24-6. Below a pressure of 5.3 atm (4,030 mm) liquid carbon dioxide does not exist. This behavior can be compared with that of water, which does not exist as a liquid if the pressure is less than 4.6 mm.<sup>1</sup>

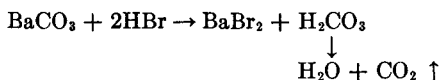
The third tube in Fig. 24-6 shows a typical condition inside a liquid carbon dioxide fire extinguisher at room temperature.

**Carbonates and Bicarbonates.** As the most abundant inorganic carbon compounds, the carbonates and bicarbonates are both useful and well-known substances. Most carbonates are only slightly soluble in water—for example, calcium carbonate,  $\text{CaCO}_3$ , barium carbonate,  $\text{BaCO}_3$ , magnesium carbonate,  $\text{MgCO}_3$ , and lead carbonate,  $\text{PbCO}_3$ . Many of the bicarbonates are stable only in water solution. Examples are calcium bicarbonate,  $\text{Ca}(\text{HCO}_3)_2$ , and magnesium bicarbonate,  $\text{Mg}(\text{HCO}_3)_2$ . All group IA metals, except lithium, form soluble salts

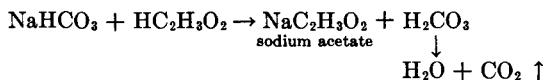
<sup>1</sup> If some liquid  $\text{H}_2\text{O}$  were thrown into a vacuum chamber in which the pressure was maintained at 4 mm, some of the liquid would evaporate instantly, thereby cooling and freezing the remaining liquid to ice. The ice would then sublime at about 0°C. Strictly speaking, this would be dry ice.

of carbonic acid, the most inexpensive and useful ones being sodium bicarbonate,  $\text{NaHCO}_3$  (baking soda), and sodium carbonate,  $\text{Na}_2\text{CO}_3$ .

Because carbonic acid is such a weak acid and is unstable, the carbonates and bicarbonates react with most acids to give  $\text{CO}_2$ . The reaction is quite rapid, and the gas is evolved readily. For instance, barium carbonate reacts with hydrobromic acid in this way:

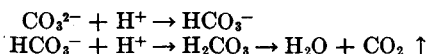


A reaction that can be tested in any kitchen occurs when sodium bicarbonate (baking soda) and acetic acid (vinegar) are combined:



The "fizz" is due to escaping carbon dioxide. Cake rises as a result of being inflated with bubbles of carbon dioxide when the baking soda,  $\text{NaHCO}_3$ , in the baking powder reacts with an acid ingredient in the baking powder. The acid component may be calcium acid phosphate,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ , sodium aluminum sulfate,  $\text{NaAl}(\text{SO}_4)_2$ , or potassium acid tartrate,  $\text{KHC}_4\text{H}_4\text{O}_6$ . The sodium bicarbonate and the acid do not react appreciably while in the dry state; but once the baking powder is in the batter, the two dissolve in the water solution and react.

All the reactions above of carbonates and bicarbonates with acids may be summarized by these equations:



As pointed out in Chap. 13, bicarbonates are amphoteric substances that can be used as buffers for solutions, because they react with both acids and bases.

Bicarbonates are unstable. When heated, they decompose to form carbonates, as described for sodium carbonate in the Solvay process in Chap. 19.

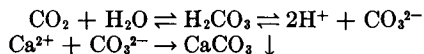
*Calcium carbonate* is one of the most widely distributed nonsiliceous minerals.<sup>1</sup> The chemistry of this simple compound is both interesting and instructive.

If carbon dioxide is passed into a solution of a cation that forms an insoluble carbonate (for example,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ , or  $\text{Pb}^{2+}$ ), a white

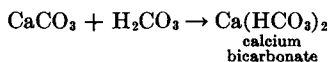
<sup>1</sup> Although we are not mainly concerned with mineral names, it is of interest to note that a mineral is named not simply on the basis of its chemical composition, but also on the basis of its general properties and appearance. For example, there are calcite, aragonite, limestone, marble, travertine, and chalk. Each of these natural substances is chiefly  $\text{CaCO}_3$ , but differences in mode of formation have caused the six to be quite different in appearance and usefulness.

## CARBON, SILICON, AND BORON

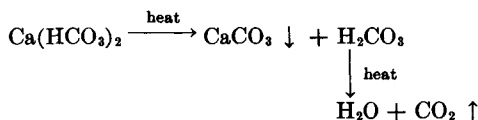
precipitate will form. Calcium carbonate precipitates when carbon dioxide is bubbled through a solution of lime water,  $\text{Ca}(\text{OH})_2$ :



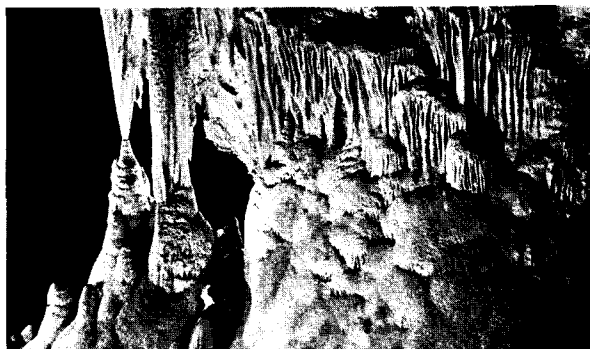
Surprisingly enough, if we continue to add carbon dioxide, the precipitate will dissolve. This is contrary to the expectation that if a little carbon dioxide causes a precipitate to form, a lot of carbon dioxide should result in even more precipitate. Actually the solid carbonate dissolves because it is reacting with carbonic acid and forming the *more soluble bicarbonate*.



If the solution of  $\text{Ca}(\text{HCO}_3)_2$  is heated, the bicarbonate decomposes and the precipitate reappears:



Or if the bicarbonate solution is simply allowed to stand in the open air, the calcium carbonate will reappear as the water evaporates:



Stalactites and stalagmites formed in Carlsbad Caverns by the precipitation of calcium carbonate. (Courtesy of Santa Fe Railway.)

FIG. 24-7

**CAVE FORMATION.** The spectacular limestone caves (such as Mammoth Cave and Carlsbad and Luray Caverns) have been dissolved out of solid rock by the gentle action of the carbonic acid formed by the solution of carbon dioxide in rain water. An original fissure or weakness in the rock probably allowed the first trickles of carbonic acid to seep through. As more and more of the carbonate was converted into the soluble bicarbonate, the hole grew in size, till there was room for an underground stream or river. Thereafter erosion by the moving water aided the dissolving action of the carbonic acid.

When the cave became open enough to allow a current of air to

## Carbon compounds

TABLE 24-4

formula	name	appearance at room conditions	remarks
$\text{CaC}_2$	calcium carbide	gray solid	reacts with water to form inflammable gas, acetylene: $\text{CaC}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{C}_2\text{H}_2$ ; used as source of this important gas
$\text{HCN}$	hydrogen cyanide	colorless gas; almond odor	poisonous gas used in pest control and in lethal gas chambers: $\text{H}_2\text{SO}_4 + 2\text{NaCN} \rightarrow 2\text{HCN} + \text{Na}_2\text{SO}_4$ (compare reaction of $\text{H}_2\text{SO}_4$ and $\text{NaCl}$ ); in laboratory keep strong acids away from cyanides
$\text{NaCN}$	sodium cyanide	white solid	solutions of sodium cyanide used to dissolve gold, silver, and platinum for electroplating baths
$\text{CS}_2$	carbon disulfide	colorless liquid; very volatile	solvent for grease, rubber, sulfur; used as solvent in preparation of rayon viscose; very inflammable, poisonous
$\text{CCl}_4$	carbon tetrachloride	colorless liquid; volatile	solvent for dry cleaning; used in fire extinguishers
$\text{CaCN}_2$	calcium cyanamide	white solid	made in one of the few nitrogen fixation processes: $\text{CaC}_2 + \text{N}_2 \rightarrow \text{CaCN}_2 + \text{C}$ ; used as is for fertilizer or hydrolyzed to yield ammonia

circulate, the most beautiful changes began to take place. Ground water saturated with calcium bicarbonate seeped through from above to the ceiling of the cave and evaporated in the circulating air. As a result of this evaporation, calcium carbonate was precipitated on the ceiling (*stalactites*). In the places where the concentrated solution dripped to the floor of the cave before evaporating, the carbonate was precipitated on the ground (*stalagmites*). (See Fig. 24-7).

**BOILER SCALE.** There are other less attractive deposits of calcium carbonate that cost us hundreds of thousands of dollars each year in heating and plumbing bills.

One of the substances usually present in hard water is calcium bicarbonate. When such water is heated in boilers or hot-water tanks, the precipitation of the calcium carbonate forms a scale in the boiler or hot-water pipes. Magnesium carbonate ( $\text{MgCO}_3$ ) also forms if magnesium bicarbonate is present in the water. Heat transfer becomes less efficient as this scale thickens. Eventually, a pipe or a boiler may become almost completely blocked with hard, rocklike carbonate scale.

**Other Compounds of Carbon.** The carbonates are just one of many important classes of inorganic compounds of carbon. Others are the cyanides, the carbides, and the carbonyls.

The cyanides are similar to the halides in many physical and chemical properties. There are simple and complex cyanides:

sodium cyanide, NaCN  
hydrogen cyanide, HCN  
potassium hexacyanoferrate(III),  $K_3Fe(CN)_6$

Examples of carbides:

calcium carbide,  $CaC_2$   
zinc carbide,  $ZnC_2$   
aluminum carbide,  $Al_4C_3$

Examples of carbonyls:

nickel carbonyl,  $Ni(CO)_4$   
iron carbonyl,  $Fe(CO)_5$

A number of especially useful compounds are listed in Table 24-4 on the preceding page.

## **COMPOUNDS OF SILICON**

**Silicon Dioxide.** Silicon dioxide, or silica, is one of the most common chemical compounds. Pure  $SiO_2$  crystals are found in nature in three polymorphic forms, the most common of which is *quartz*. Sand, agate, onyx, opal, amethyst, and flint are silicon dioxide with traces of impurities.

Fused quartz is used to make crucibles and other laboratory vessels that must be heated to extremely high temperatures. Not only does it have a high softening point (about  $1500^\circ C$ ) but another equally valuable property is its very low coefficient of thermal expansion. A substance with a high coefficient of thermal expansion expands and contracts a great deal when heated and then cooled. Quartz expands very little when heated; therefore, it is not likely to crack even if it is cooled rapidly and unevenly.

The forms of silica are some of the truly important crystal structures, not only because silica itself is such an abundant and useful substance, but because the  $(SiO_4)$  structure is the fundamental unit in most minerals. As is evident in Fig. 24-3,  $SiO_2$  crystals have two main features: (1) each silicon atom is at the center of a tetrahedron of four oxygen atoms, and (2) each oxygen atom is midway between two silicon atoms. One way of looking at the quartz structure is to picture the tetrahedron  $(SiO_4)$  as in Fig. 24-8 and then picture each of the oxygens as a member of another tetrahedron. Billions upon billions of such tetrahedra are tightly linked, in three dimensions, in each grain of sand on the beach or in the desert.

Attention is often called to the great differences between  $SiO_2$  and  $CO_2$  in physical properties. The former does not soften till heated to about  $1500^\circ C$ ; the latter sublimates at  $-78^\circ C$ . This and other differ-

Four ways of representing  
( $\text{SiO}_4$ ) tetrahedra in silica and  
silicates.

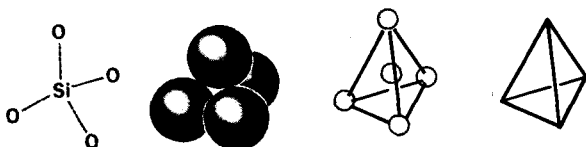
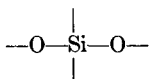


FIG. 24-8

ences can be correlated with the type of molecule, which in turn depends on the type of bond,  $\text{Si}-\text{O}$  single bonds or  $\text{C}=\text{O}$  double bonds.

Carbon unites with oxygen by forming two covalent bonds with each oxygen,  $\text{O}=\text{C}=\text{O}$ . Carbon dioxide is made up of tiny triatomic molecules and is a gas at room temperature. In contrast, the endless



structure in silicon dioxide, Fig. 24-3, is a single molecule, whether a grain of sand or a magnificent quartz crystal larger than a man's head.

Silicon dioxide is an acidic oxide. Though it is practically insoluble in water, it does dissolve in such bases as sodium hydroxide. One of the few other compounds that attacks it is hydrogen fluoride, which reacts to produce the volatile substance  $\text{SiF}_4$ .

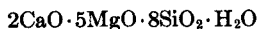
**Silicates.** A few of the many thousand *mineral silicates* that are known were listed in Table 24-2. The following ideas will help us relate the many silicates to one other.

1. Note how often aluminum is present in silicates. It is the third most abundant element in the earth's crust. Other elements present in the examples in Table 24-2 are iron, calcium, sodium, potassium, and magnesium. Any of them is likely to be found in silicate minerals.

2. The formula of any silicate can be written as a "resolved formula," that is, as a series of simple formulas. For example, the formula of anorthite,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ , can be resolved into a series of simple oxide formulas:



Similarly, that for tremolite,  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ , can be resolved into



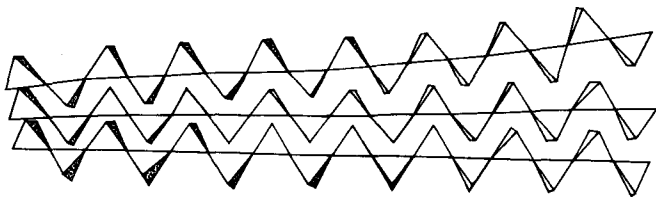
Artificial silicates can be made by melting together a mixture of basic oxides and silicon dioxide.

The resolved formulas emphasize the fact that no matter how complicated the formulas are, the total positive oxidation states must equal the total negative oxidation states.

3. Neither the resolved formulas nor the collected formulas represent molecules; they only show the relative number of particles in the huge silicate molecules.



FIG. 24-9



Asbestos is a silicate in which the molecules form long chains of  $(\text{SiO}_4)$  tetrahedra. (Photograph courtesy of Johns-Manville.)

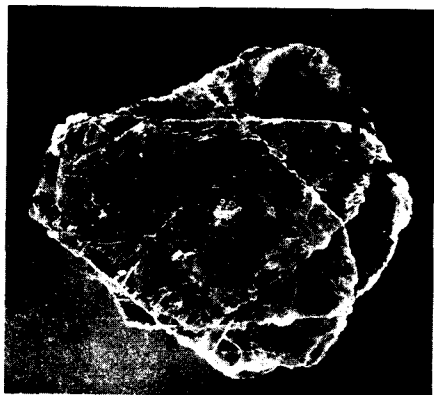
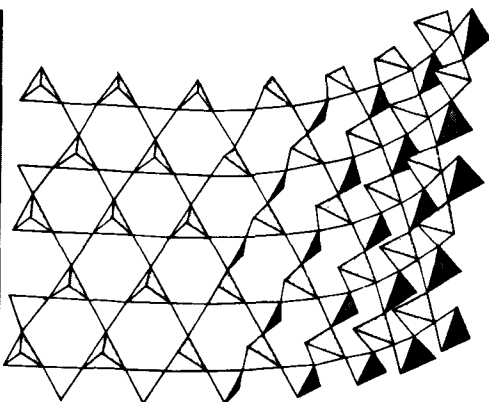


FIG. 24-10

Micas are silicates in which the molecules form layers of  $(\text{SiO}_4)$  tetrahedra.



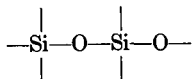
4. The huge silicate molecules tend to link themselves together as chains (amphiboles or pyroxenes, as in Fig. 24-9), as layers (micas, as in Fig. 24-10), or as a boxlike framework (feldspars). In any of these, the  $(\text{SiO}_4)$  tetrahedron is a principal building unit.

5. Ions other than silicon and oxygen, such as  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{OH}^-$ , are often found tucked into holes in the main structure. Also, very small cations (especially  $\text{Al}^{3+}$ ) may be substituted in place of  $\text{Si}^{4+}$ , and small anions in place of  $\text{O}^{2-}$ .

The presence of varying amounts of these substitute ions is what made the study of the silicates so difficult for a long time. Till X-ray diffraction and the electron microscope enabled the scientist to determine the placement of the various ions, chemical analyses gave an incomplete picture of the structure of these compounds.

## FAMILIAR SILICON-CONTAINING MATERIALS

Two of man's oldest industries are pottery and brick making. Sometime later he learned to make mortar, plaster, and cement. In spite of having mastered the art of cement and ceramics long ago, we still know relatively little about the science of these important materials. However, the knowledge we do have indicates that the



bonds are probably responsible for the strength of both cement and ceramics.

**Ceramics.** Ceramic products are made of mixtures of various finely divided minerals and rocks that will form a strong rocklike mass when heated to a high temperature. The most important ingredient is *clay*, a naturally occurring material that is formed by the action of the weather upon certain feldspars. Although clay is not a pure substance, it is chiefly *kaolinite*,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , a soft, easily pulverized mineral. Kaolinite is a hydrated aluminum silicate.

**Cement.** Cement is a material whose rocklike strength is due to silicon-oxygen bonds. It becomes hard as the result of a low temperature reaction, instead of the high temperature used in the ceramic kiln.

Portland cement, first made in the early 1800s in England (and named for its similarity to a natural rock mined on the Isle of Portland), can be made from limestone, clay, and gypsum. Other materials, such as blast furnace slag or iron ore, may be used, depending partly on what is available in the locality of the cement plant.

**Glass.** The glassy state is something between the true crystalline solid and the liquid state. Unlike a crystalline material, glass does not have a sharp melting point but begins to soften far below the temperature at which it flows like a liquid.

At temperatures slightly above the softening point, glass can be bent easily into almost any desired shape. At somewhat greater temperatures, when it begins to behave like a very viscous liquid, small pieces of the molten glass are drawn into spherical drops by surface tension, and two pieces of molten glass will join and become a single piece. In this melted condition it can be blown, molded, or rolled into sheets.

Figure 24-11 compares a hypothetical crystalline and a glassy structure. The building units are roughly the same; but in the crystal they are arranged with perfect symmetry, whereas in the glass they have a random arrangement and are distorted.

Although it appears to be rigid and brittle, glass will bend at room temperature if put under strain and will eventually be deformed, taking a new shape till the stress is relieved. Filaments of glass bend so



## CARBON, SILICON, AND BORON

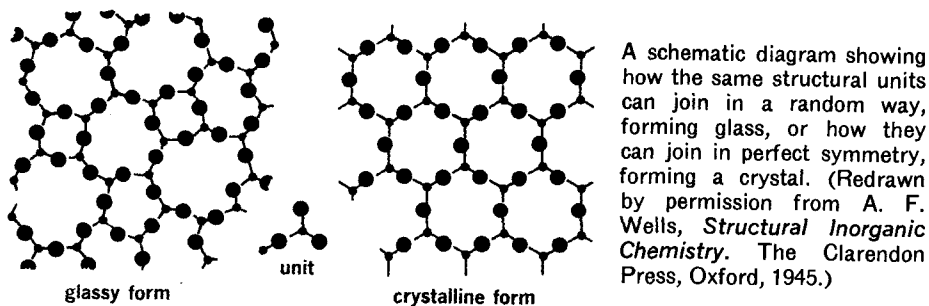


FIG. 24-11

readily that they can be spun into cloth; encased in plastic, they are used to make the important new structural material fiberglass.

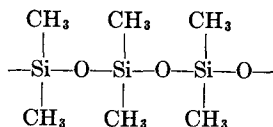
Glass is so inexpensive and common that it is surprising to learn that the glassy state is really quite rare. Only one element (selenium), a few oxides (such as  $B_2O_3$ ,  $SiO_2$ ,  $GeO_2$ , and  $P_2O_5$ ), and a few oxy-salts (such as the borates, silicates, and phosphates) exist in a glassy form. Neither simple ionic nor simple molecular substances form glasses.

*Lime glass*, exceeding all other types in tons produced, is used as window glass, plate glass, and bottle glass. It is essentially a mixture of sodium and calcium silicates, with an excess of silica.

*Pyrex* is a borosilicate glass with a very low coefficient of thermal expansion, hence its wide use for cooking and serving utensils. Moreover, it can be shaped and blown by amateur glassblowers. For this reason, Pyrex is a great boon to research chemists and physicists who often need to make special glass equipment.

Hundreds of different glasses are made: *lead glass* for fine cut glassware; *colored glass* for beauty (for example, selenium or gold added to make it red; cobalt compounds for blue; chromium or copper compounds for green); *tempered glass* for great strength.

*Silicones*. Some of the most interesting synthetic compounds, unlike anything found in nature, are the *silicones*. These substances are chainlike molecules of Si, O, C, and H atoms. Methyl silicone,<sup>1</sup> shown in the formula below, is an example:



As the molecular weight changes, the properties change. A silicone made of short chain molecules is an oily liquid; silicones with medium-length chains behave as viscous oils, jellies, and greases; those with very long chains have a rubberlike consistency.

<sup>1</sup> The methyl group,  $-\text{CH}_3$ , is the simplest carbon-hydrogen group that can be added to the side of the Si atom. For the formulas of more complex groups, such as  $-\text{C}_2\text{H}_5$ , ethyl,  $-\text{C}_3\text{H}_7$ , propyl, see Chap. 25.

Other useful properties of the silicones are their resistance to chemical attack and their water-repellent nature (that is, they are *hydrophobic*). Textiles and wood and metal surfaces can be water-proofed with a thin silicone coating; furthermore, it is tough and long-lasting.

**Zeolites.** The *zeolites* are a class of silicate minerals in which a pair of ions—for example,  $\text{Al}^{3+}$  and  $\text{K}^+$ —has been substituted for one  $\text{Si}^{4+}$ . The trivalent  $\text{Al}^{3+}$  takes the place of the  $\text{Si}^{4+}$  in the center of an  $\text{SiO}_4^{4-}$  tetrahedron, and the monovalent  $\text{K}^+$  fits nearby in a hole in the crystal structure. Figure 24-12 shows the structure of *natrolite*, a zeolite in which  $\text{Na}^+$  ions fit in the holes; the formula can be written  $\text{Na}_2(\text{Al}_2\text{Si}_3\text{O}_{10}) \cdot 2\text{H}_2\text{O}$  to emphasize the freedom and ionic character of the sodium ions. The zeolites are characterized by a porous structure through which water can circulate rather freely.

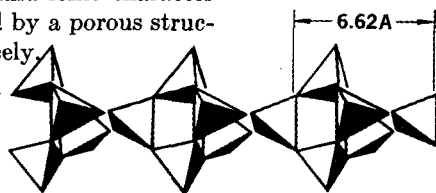


FIG. 24-12

A possible arrangement for the naturally-occurring zeolite *natrolite*,  $\text{Na}_2(\text{Al}_2\text{Si}_3\text{O}_{10}) \cdot 2\text{H}_2\text{O}$ . Each colored tetrahedron has an Si atom at the center, whereas each gray one has an Al atom. The order in the natural crystal is not necessarily so regular as here, but the ratio is 3:2. Chains like this are crosslinked with others in three dimensions;  $\text{Na}^+$  ions and water molecules fit into holes in the lattice.

The great use of the zeolites is in water softening. Certain ions, such as calcium and magnesium, are objectionable in water, because they form insoluble precipitates (curd or scum) with soaps. When water is allowed to trickle slowly through a bed of crushed zeolite, the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in solution tend to be attracted to the mineral;  $\text{K}^+$  or  $\text{Na}^+$  ions leave the zeolite and take the place of the divalent ions in solution. (One  $\text{Ca}^{2+}$  ion will displace two  $\text{K}^+$  ions.) Such a process is called **ion exchange**. In this way  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions are exchanged for the unobjectionable  $\text{Na}^+$  and  $\text{K}^+$  ions.

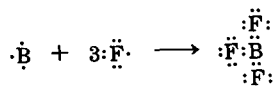
## COMPOUNDS OF BORON

Boron compounds are obviously much less important than silicon compounds because of the difference in abundance of the two elements. On the basis of known similarities in structure, it is thought that the borates resemble the silicates in variety and complexity. Borate anions of several types have been discovered—discrete ions, chains, rings, and layer structures. Borax, the most important natural compound, is found in desert areas where it has been precipitated by the evaporation of salt lakes.

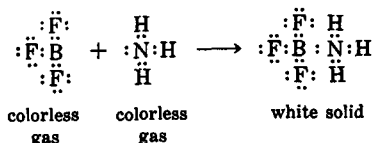
Like carbon and silicon, boron tends to form covalent rather than ionic bonds. Because a boron atom has only three electrons in its

## CARBON, SILICON, AND BORON

outside shell, it can form three covalent bonds and still not have a complete outside shell of eight electrons. Consider the formation of boron trifluoride:



In  $\text{BF}_3$  boron has only six bonding electrons. This compound (and others like it) has such a strong attraction for another electron pair that it combines with some molecules that have an electron pair to share.<sup>1</sup>  $\text{BF}_3$  combines with  $\text{NH}_3$  in this way,  $\text{BF}_3$  behaving as a typical Lewis acid and  $\text{NH}_3$  as a Lewis base:



## CHAPTER REVIEW

### Topics

Chemical and physical properties of carbon, silicon, and boron; preparation of different forms of carbon, structures of silicates, combustion of common fuels, chemistry of carbonates and bicarbonates, resolved formulas, ceramics, cement, zeolites, ion exchange.

### Exercises

- What types of experimental evidence indicate that the bonding of atoms in graphite differs from that in diamond?
  - Suggest a way of showing that the bond energy in graphite differs from that in diamond.
- Diagram electron-dot formulas for silicic acid and metasilicic acid.
- In a solution of sodium orthosilicate litmus is blue. Write an equation to explain this observation.
- Describe the complete sublevel electronic structures for carbon, silicon, and boron. Why do they not tend to form simple cations?
- Silica gel used in dehumidifiers is sometimes colored with a substance so that it is blue when dry, becoming pink as it becomes saturated with moisture. Describe what type of substance might serve as such a color indicator and identify a certain compound that could so serve.
- What are some structural similarities between diamond and silica?
- Outline a possible series of natural processes by which carbon in atmospheric carbon dioxide could eventually become diamond.

<sup>1</sup> When two atoms are joined by a shared pair of electrons and both the electrons have been contributed by one of the atoms, the bond is called a *coordinate covalent bond*.

8. What are some large-scale chemical processes mentioned in previous chapters that utilize graphite?
9. Silica gel and boneblack can be used in somewhat similar ways. Explain.
10. Phosphorus is one of the few substances recognized as elements today that were known to the alchemists of old. Explain with equations how phosphorus might have been prepared from bones (and any other common materials needed).
11. *a.* Write a hypothetical equation for the formation of carbon black.  
*b.* Explain the action of a Cottrell precipitator in collecting carbon black. What other type of separating process might possibly be used to collect carbon black?
12. Do you think silicon was one of the substances known to ancient man? Why?
13. A silicate, for example wollastonite in Table 24-2, can be dissolved by mixing with sodium carbonate, heating sufficiently to fuse the mixture, then cooling, and treating with nitric acid. Write equations for possible reactions.
14. Explain, using a crude diagram, the mechanism whereby carbon monoxide poisons a person.
15. It has been claimed that cigarette smoking can interfere with physical and mental activity by decreasing the amount of oxygen available to the cells. Can you suggest possible chemical reactions consistent with this claim?
16. Calculate the heat energy released by the combustion of 10.0 liters of a 50:50 mixture of carbon monoxide and carbon dioxide.
17. Calculate the change in enthalpy for the reduction of a mole of carbon dioxide by carbon. Is the reaction exo- or endothermic?
18. Calculate the change in enthalpy per mole of iron produced when iron(III) oxide is reduced by carbon monoxide. Is the reaction exo- or endothermic?
19. Two open 500-ml beakers of the same weight are placed on the pans of a balance. If one is filled with gaseous carbon dioxide, what is the difference in weight of the two beakers?
20. A demonstration similar to that described in Exercise 19 can be done with hydrogen if the beakers are suspended upside down from the arms of a balance. If one beaker is filled with gaseous hydrogen, what is the difference in weight of the two beakers?
21. In coal gas there is a measurable amount of carbon monoxide but hardly any carbon dioxide. Explain this on the basis of probable chemical reactions, assuming that a small amount of oxygen is available.
22. *a.* Suppose a company had as a waste product a large volume of dilute sodium hydroxide solution that it wished to neutralize before discharging it into a nearby river. Would it be possible to neutralize the solution by bubbling through it exhaust gases formed by burning coal? Explain with equations.  
*b.* Repeat (*a*) for a waste product of calcium hydroxide solution.

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23. Calculate, using data from Table 16-1 and Table 1 of the Appendix, the heat value in Btu per cubic foot, at 25°C and 1 atm, of a producer gas that is 30 per cent by volume CO, 10 per cent H<sub>2</sub>, and 60 per cent N<sub>2</sub>.
24. When liquid carbon dioxide issues from a fire extinguisher, some of it turns to gas, some to solid. Explain.
25. A common type of fire extinguisher contains a water slurry of sodium bicarbonate and a loosely stoppered bottle of sulfuric acid. When turned upside down, the extinguisher is activated and a stream of liquid is emitted through a hose. Explain the action, using appropriate equations.
26. "A carbonate rock is easily identified by testing it with acid."
  - a. Write a chemical equation for the test and describe the visible results.
  - b. Might not a sulfide rock give similar visible results? Explain with a chemical equation.
  - c. Could the carbonate be distinguished from the sulfide rock by the acid test? Explain.
27. Calcium carbonate is more soluble in rain water than in absolutely pure water. Explain this action with balanced equations.
28.
  - a. Show, with at least four specific balanced equations, the amphoteric character of sodium bicarbonate.
  - b. On the basis of the equations that you have just written, explain why a solution of sodium bicarbonate is often kept handy in chemical laboratories as a safety precaution.
29. In localities where the soil tends to be acidic, crushed limestone is often applied regularly by farmers to "sweeten" the soil.
  - a. Why might a soil be acidic?
  - b. Why would limestone lessen this acidity?
  - c. How is the term "sweeten" appropriate for this treatment?
30. If one blows his breath into lime water through a straw, the liquid becomes milky and turbid. If the blowing is continued for some time, the liquid becomes a clear solution again. Explain with equations.
31. Suppose a home hot-water tank is heated with an electric immersion rod. Is a scale of calcium carbonate more likely to form in the water entry pipe, on the rod, on the walls of the tank, or in the water exit pipe?
32. Calcium carbide has long been used as the source of gas for emergency lamps or miners' lamps. Write equations and account for the generation of light.
33. If potassium cyanide is dissolved in a sodium hydroxide solution, the vapors from the solution are not dangerous; but if the cyanide salt is dissolved in a hydrochloric acid solution, the vapors from the solution are dangerous. Explain with equations.
34. Discuss the physical and chemical differences between the dioxides of carbon and silicon.
35. A fire-resistant cloth can be woven from certain silicates. What features make this possible?

36.
  - a. Write a resolved formula for kaolinite.
  - b. Write resolved formulas for some of the silicates in Table 24-2.
37. How would you go about trying to prepare a sample of synthetic sodalite?
38. Calcite is a transparent, potentially cheap material. Suggest some of the reasons why it is not widely used in place of glass.
39. How could one analyze a sample of glass to determine if it had lead in it?
40. Ammonium fluoride is easily decomposed into two compounds. Write an equation for the decomposition and explain the use of ammonium fluoride to etch glass.
41. Consider one of the single hexagons in the crystalline form of Fig. 24-11. By assigning partial occupancy in that hexagon to each of the twelve particles bordering the hexagon, show how the ratio of 2:3 for the two types of particles can be calculated.
42. Zirconium and hafnium, which are so similar to one another physically and chemically, can be separated by ion exchange. Describe how this might be done.
43. An unskilled glass worker may be able to heat and successfully reshape a tumbler made of Pyrex glass, but not one of ordinary glass. Why?
44. Name two industrial processes, discussed in this or previous chapters, that take advantage of each of the following concepts; write an equation for each reaction involved:
  - a. Precipitation of an insoluble product followed by filtration
  - b. A chain reaction in the gas phase
  - c. A solid catalyst for gaseous reactants
  - d. Electrochemical oxidation and reduction
  - e. A by-product of a process being used at an early step in the same process
  - f. The heat evolved in a necessary reaction being used as a source of heat energy
  - g. Use of special corrosion-resistant materials
  - h. Plants located near sources of raw materials or energy
45. Show how the use of ammonium nitrate as a fertilizer in mica-containing soil could increase the supply of available potassium.
46. Write equations for the following reactions:
  - a. Boron and fluorine
  - b. Fused silica and iron(II) oxide
  - c. Fused magnesia, lime, and silica
  - d. Reaction of  $\text{BF}_3\text{NH}_3$  as an acid dissolved in liquid ammonia
  - e. Reaction of boron trichloride and gaseous ammonia
47. Boron is in the same family as the metals gallium, indium, and thallium. They are malleable and ductile and form basic oxides. Compare these properties with those of boron. Explain the differences on the basis of atomic structure. Is the relation of boron to the other members of group IVA unlike the relation of some other elements to other members of their families? Discuss fully.

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# ORGANIC CHEMISTRY;

## HYDROCARBONS



*Organic Chemistry.* The early chemist drew a sharp distinction between the compounds that form the rocks and soils and the compounds that originate during the growth of plants and animals. In his view, the latter came into being only through some vital force associated with life processes; their synthesis in the laboratory was impossible. Accordingly, he referred to them as **organic** compounds to distinguish them from the earthy compounds, which he called **inorganic** compounds.

The development of laboratory procedures for analyzing and synthesizing compounds during the first half of the nineteenth century enabled chemists to learn a great deal about organic compounds. They were able to synthesize the simple ones in the absence of a "vital force"<sup>1</sup> and to show that the same laws and principles apply to both types of compounds.

Since the first organic compound was synthesized in the laboratory, a tremendous effort has been made to isolate, identify, and synthesize all the compounds that originate in plants and animals. This has been; and is, a most important type of research, for organic compounds constitute all or a major portion of petroleum, coal, proteins, fats, carbohydrates, vitamins, hormones, cellulose, anesthetics, antiseptics, antibiotics, enzymes, and a host of other useful products.

Although perhaps most of the natural organic compounds have been isolated and characterized, man has not been able to synthesize some of the more complex ones. An interesting and important outcome of this work has been the synthesis of a large number of com-

<sup>1</sup> In 1828, the German chemist Wöhler synthesized urea by heating ammonium cyanate. Previously (1824) he had synthesized oxalic acid from cyanogen. Because of this work, Wöhler is usually given credit for initiating the downfall of the "vital force" idea.



pounds that do not originate in living organisms but are very similar in composition and properties to those which do. Inasmuch as both the natural and synthetic compounds contain carbon, we now define **organic compounds** as the *compounds of carbon*.<sup>1</sup> No distinction is made between those of natural origin and those of synthetic origin. **Organic chemistry** is the science that deals with carbon compounds.

*Number of Organic Compounds.* The number of organic compounds has been estimated recently at well over a million. This is many times more than the number of known compounds that do not contain carbon. The large number of carbon compounds is explained on the basis of two characteristics of carbon atoms: (1) Carbon atoms unite with one another by sharing one or more pairs of electrons to form chain or ring molecules. (2) Carbon atoms, with four valence electrons, can form four covalent bonds. This means that the carbon atoms are able to form rings and chains and still have valence electrons left over that can be used to form bonds with atoms of other elements.

The other group IVA elements—silicon, germanium, tin, and lead—also have four valence electrons. However, their outer-shell electrons are located progressively farther from the nucleus with increasing atomic number and are less strongly held. Hence, these elements are more metallic than carbon and are less likely to form chain or ring molecules by means of covalent bonds. Silicon, which is next to carbon in the family, does form compounds in which silicon atoms are joined in chains, but these chains are neither long nor very stable.

## FOUR SERIES OF HYDROCARBONS

**Hydrocarbons** are defined as compounds that contain only carbon and hydrogen. Hydrocarbons occur abundantly in nature, largely as petroleum, natural gas, and coal. Thousands are known; the number theoretically possible is virtually without limit. They are of special importance to the student of chemistry, because they are the basis for the systematic naming and classification of organic compounds.

We shall confine our study largely to four classes or series: the **alkanes**, the **alkenes**, the **alkynes**, and the **benzene (aromatic) hydrocarbons**. The first three series are frequently referred to collectively as the **aliphatic hydrocarbons**.<sup>2</sup>

*Alkanes.* The alkane series is also called the *methane* hydrocarbons or the *paraffins*. The first few members are listed in Table 25-1.

<sup>1</sup> As previously pointed out, there are certain rocklike or earthy carbon-containing substances that are usually classed as inorganic compounds, for example, the carbonates, carbides, and cyanides.

<sup>2</sup> The molecules of aliphatic hydrocarbons are characterized by carbon chains (an important exception is the cycloalkane group), whereas those of the aromatic hydrocarbons are characterized by carbon rings and a bond system similar to that of benzene.

The number of carbon atoms, beginning with the pentanes, is indicated by the Greek prefix, except that occasionally the Latin is used, that is, *nona* or *non* for nine.

*Alkanes* ( $C_nH_{2n+2}$ , general formula)

TABLE 25-1

CH <sub>4</sub>	methane	C <sub>5</sub> H <sub>12</sub>	pentanes (3)	C <sub>9</sub> H <sub>20</sub>	nonanes (35)
C <sub>2</sub> H <sub>6</sub>	ethane	C <sub>6</sub> H <sub>14</sub>	hexanes (5)	C <sub>10</sub> H <sub>22</sub>	decanes (75)
C <sub>3</sub> H <sub>8</sub>	propane	C <sub>7</sub> H <sub>16</sub>	heptanes (9)	C <sub>15</sub> H <sub>32</sub>	pentadecanes
C <sub>4</sub> H <sub>10</sub>	butanes (2)*	C <sub>8</sub> H <sub>18</sub>	octanes (18)		(4,347)

\*The numbers in parentheses are the calculated numbers of possible isomers for the individual molecular formulas. In the cases of the larger molecules no attempts have been made to isolate all the isomers. For example, C<sub>20</sub>H<sub>42</sub> has 366,319 possible different structural arrangements.

Note that the molecules of each member differ from those of the preceding and succeeding members by a constant number of atoms (1 carbon and 2 hydrogen atoms). Such a series is called a **homologous series**, and each member is a **homolog** of the series. Furthermore, a general formula can be assigned to the series that will represent any member. For the alkanes, the general formula is  $C_nH_{2n+2}$ , where  $n$  is the number of carbon atoms. For example, if the molecule of a homolog contains 100 carbon atoms,  $n$  is 100 and  $2n + 2$  is 202. The formula is C<sub>100</sub>H<sub>202</sub>.

**Alkenes.** The alkene series is also referred to as the *ethylene* series. The first few members are

$C_nH_{2n}$ , general formula

C <sub>2</sub> H <sub>4</sub>	ethene (ethylene)	C <sub>4</sub> H <sub>8</sub>	butenes (3)
C <sub>3</sub> H <sub>6</sub>	propene (propylene)	C <sub>5</sub> H <sub>10</sub>	pentenes (5)

**Alkynes.** The alkynes are also referred to as the *acetylene* series. The first few members are

$C_nH_{2n-2}$ , general formula

C <sub>2</sub> H <sub>2</sub>	ethyne (acetylene)	C <sub>4</sub> H <sub>6</sub>	butynes (2)
C <sub>3</sub> H <sub>4</sub>	propyne	C <sub>5</sub> H <sub>8</sub>	pentynes (3)

**Aromatic Hydrocarbons.** There are many homologous series of aromatic hydrocarbons, the most important ones being derived from benzene, C<sub>6</sub>H<sub>6</sub>. We shall give most of our attention to the series that can be represented by the general formula  $C_nH_{2n-6}$ :

C <sub>6</sub> H <sub>6</sub>	benzene	C <sub>8</sub> H <sub>10</sub>	xylenes (3) and ethyl benzene
C <sub>7</sub> H <sub>8</sub>	toluene	C <sub>9</sub> H <sub>12</sub>	8 isomers

## STRUCTURE OF HYDROCARBON MOLECULES

In accounting for the large number of organic compounds, it was pointed out that a carbon atom could form four bonds with other atoms, including other carbon atoms. Another distinctive feature of carbon atoms is their capacity for combining with one another via different types of bond hybridization. For example, the carbon atoms in alkane molecules are joined by  $sp^3$  bonds (see Chap. 4). Some of the carbon atoms in molecules of the other series, except for the first member of each, may also be joined by  $sp^3$  bonds, but each molecule of an alkene, alkyne, or benzene hydrocarbon has at least two carbon atoms joined by bonds which represent a different kind of orbital hybridization and which endow the hydrocarbons of that series with the properties characteristic of the series.

*Structure of Alkane Molecules.* A striking characteristic of the bonds in alkane hydrocarbons is their *equivalence*. For example, the four carbon-hydrogen bonds in methane,  $\text{CH}_4$ , are identical in reactivity and stability. Moreover, the valence forces are uniformly directed from the carbon atom toward the corners of an imaginary tetrahedron at angles of  $109^\circ 28'$ . It is difficult to account for these characteristics in terms of valence orbitals of the most stable state of an isolated carbon atom, a state in which it is thought that two of the four valence electrons occupy the  $2s$  orbital as paired electrons and that each of the remaining two occupies separate  $2p$  orbitals. Instead, as pointed out in Chap. 4, it is believed that, in compound formation of the alkane type, one of the  $2s$  electrons is elevated into a vacant, higher-energy  $2p$  orbital to provide four orbitals with four unpaired electrons (see Fig. 4-8). In the process, the resulting orbitals become identical in all respects and are directed outward from the nucleus at  $109^\circ 28'$  angles. Because they result from the blending or hybridization of one  $s$  and three  $p$  orbitals, they are referred to as  $sp^3$  orbitals. The energy required to promote an  $s$  electron to a  $p$  orbital is thought to be more than balanced by the energy liberated in forming four equivalent bonding orbitals in the resulting alkane molecule.

In the formation of methane, each  $sp^3$  orbital is thought to interpenetrate the  $s$  orbital of a hydrogen atom; that is, each hydrogen atom is bonded to carbon by a sigma bond involving an  $s$  orbital of hydrogen and an  $sp^3$  hybrid orbital of carbon (see Fig. 25-1a). This results in a tetrahedrally shaped molecule with the four hydrogen nuclei at the four corners and the carbon nucleus at the center. Because carbon and hydrogen have electronegativities of 2.5 and 2.1, respectively, we might expect the carbon-hydrogen bond to be somewhat polar, with the electron cloud slightly displaced toward carbon. The properties of the alkanes show that this is correct. However, the symmetrical shapes of most alkane molecules have the effect of balancing the partial charges, so that the molecules as a whole are

A schematic representation of the bonding orbitals in: (a) methane molecule; (b) ethane molecule.

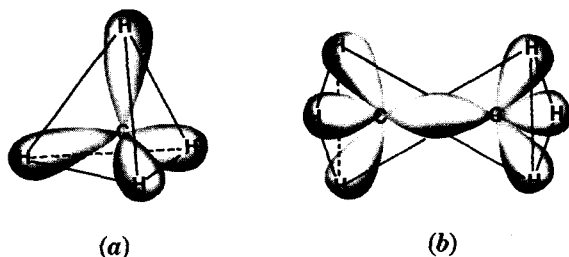


FIG. 25-1

The bonding orbitals in a propane molecule.

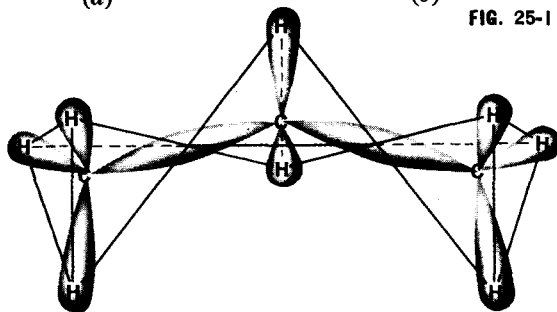


FIG. 25-2

nonpolar. For example, the dipole moments of methane and ethane are zero.

In an ethane molecule, C<sub>2</sub>H<sub>6</sub>, two carbon atoms are joined by a sigma bond formed by the overlap of an *sp*<sup>3</sup> orbital from each carbon atom (Fig. 25-1b). The six hydrogen atoms, three to each carbon, are bonded to carbon by sigma bonds in the same manner as in methane.

In propane molecules, C<sub>3</sub>H<sub>8</sub>, three carbon atoms are joined by sigma bonds formed by the overlap of *sp*<sup>3</sup> orbitals (Fig. 25-2). Because *sp*<sup>3</sup> bonding orbitals lie along axes that form 109°28' bond angles with one another, the lines that connect the three carbon nuclei form the same angle.

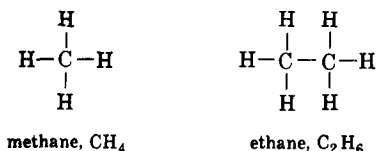
The carbon atoms in molecules of butane, pentane, hexane, and, as a matter of fact, all alkanes, are thought to be joined by sigma bonds of the same type shown for ethane and propane in Figs. 25-1 and 25-2. The hydrogen atoms are also bonded by sigma bonds in the same manner as described for methane.

**SIMPLE STRUCTURAL FORMULAS.** Molecular formulas, that is, ones that show only the number and kind of atoms in molecules, such as C<sub>6</sub>H<sub>12</sub> and C<sub>6</sub>H<sub>14</sub>, are generally inadequate for the following reasons. (1) Unless the molecule is small, the molecular formula represents more than one compound. The numbers in parentheses in Table 25-1 show the possible number of hydrocarbons that may have the particular molecular formula. (2) The molecular formula is of little value in correlating and classifying properties, and (3) it offers no clue as to how the compound can be synthesized.

The very detailed structural formulas shown in Figs. 25-1 and 25-2

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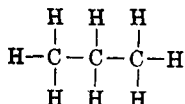
require too much space and are too difficult to reproduce for the representation of the structures of a million-odd organic molecules. Long before such detailed information was available, as far back as about 1850, the organic chemist had worked out experimentally the relative positions of atoms in certain molecules. Gradually, a simple type of structural formula was developed for showing this kind of information, a graphic representation in which each symbol represents an atom of the element, and one short line represents a single pair of shared electrons (a covalent bond). In the following structural formulas, note that four valence bonds are formed by each carbon, whereas each hydrogen atom forms only one bond:



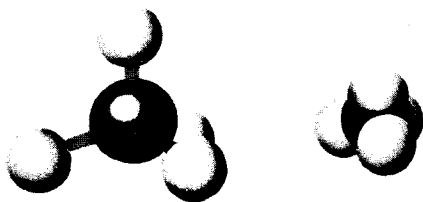
The structure may also be shown by using dots to represent a pair of shared electrons, as in earlier chapters:



The structural formula for propane is



**LIMITATIONS OF STRUCTURAL FORMULAS.** The formulas above do not show the correct positions of the atoms in space. For example, they seem to indicate that all the atoms are in one plane and that the bond angles are either  $90^\circ$  or  $180^\circ$ . In spite of these drawbacks, simple structural formulas that employ lines for valence bonds and



Two methods of representing the spatial arrangement of the atoms in a molecule of methane. Left, a ball-and-stick model. Right, a model which shows the relative sizes of the atoms as well as their positions in space.

**FIG. 25-3**

symbols for atoms are universally used to represent organic molecules. When the occasion demands, we interpret them in terms of spatial relationship of atoms, bond angles, and bonding orbitals.

When it is desirable to represent the spatial arrangement of atoms in molecules, three-dimensional diagrams and models, such as are shown in Figs. 25-3 and 25-4, are often used.

Ball-and-stick models of ethane and propane. Each stick represents one covalent bond and each ball an atom (dark for carbon and light for hydrogen).

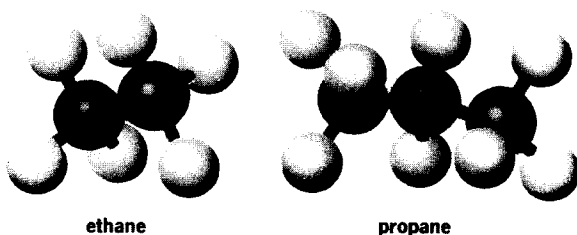
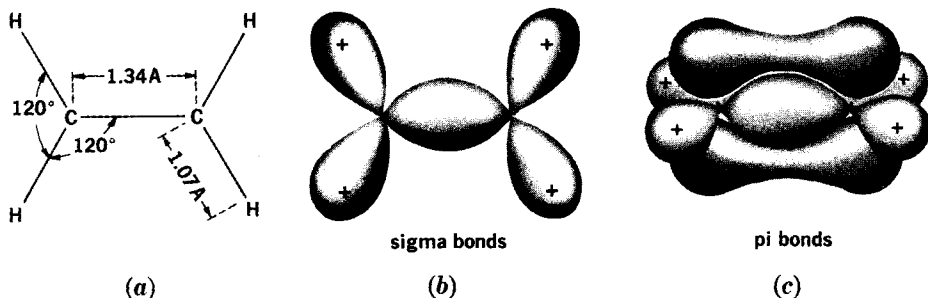


FIG. 25-4

**Structure of Alkene Molecules.** Alkene molecules ( $C_nH_{2n}$ ) have two hydrogen atoms less than the corresponding alkane molecules ( $C_nH_{2n+2}$ ), except that an alkene corresponding to methane and having the formula  $CH_2$  does not exist. Apparently, at least two carbon atoms must be present in an alkene molecule to allow a special kind of bond hybridization that brings stability to the molecule. Let us examine proposed structures for the first two members, ethene and propene, to see the type of bonding that is believed to exist.

Measurements show that the bond angles in ethene are not  $109^\circ 28'$  but approximately  $120^\circ$ , as shown in Fig. 25-5a, and that the molecule is planar. Moreover, the distance C-C is 1.34 Å as compared with 1.54 Å in ethane. These facts suggest that all the bonds in ethene are different from the  $sp^3$  bonds of ethane. It is thought that one  $s$  and only two  $p$  orbitals hybridize to form three equivalent  $sp^2$  bonding orbitals, which extend toward the corners of an equilateral triangle, with the carbon nucleus at the center (the remaining  $p$  orbital with its one electron will be dealt with in the next paragraph). Two hydrogen atoms are then bonded to a carbon atom, each by a sigma bond



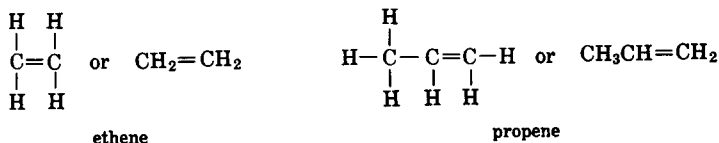
Schematic representation of the structure of an ethene molecule: (a) bond angles and positions in space of the C and H nuclei; (b) sigma bond between carbons and sigma bonds between hydrogen and carbon; (c) pi bond between carbons (note that the molecule has been rotated almost  $90^\circ$  so that the C and H nuclei are in a plane almost perpendicular to the plane of the paper.)

FIG. 25-5

resulting from the overlap of a hydrogen  $s$  orbital and a carbon  $sp^2$  orbital. The two carbon atoms are bonded (in part) by the overlap of the remaining  $sp^2$  orbital of each. This much of the structure of ethene is shown in Fig. 25-5b.

The remaining  $p$  orbital of each carbon atom contains one electron and lies above and below the plane of the  $sp^2$  bond orbitals with the axis of its lobes perpendicular to this plane; the two axes are parallel to one another (Fig. 25-5c). Because of the nearness of the two carbon atoms, the  $p$  orbitals overlap laterally (along the edges rather than head-on) to form a second bond, called a  $\pi$  bond, between the two carbon atoms (Fig. 25-5c). Thus, the carbon atoms in ethene can be thought of as being joined by a *double bond* consisting of a sigma bond and a  $\pi$  bond (Fig. 25-5d). Thermochemical measurements of bond energies reveal that the energy of the double bond in ethene is not twice that of the sigma C-C bond in ethane, a fact that indicates that the  $\pi$  bond is a weaker bond than the sigma bond.

The bonding system that we have discussed for ethene is thought to exist for one pair of carbon atoms in the molecules of all ethene homologs, the remaining atoms being bonded as in the alkanes. The double bond is usually shown in structural formulas by a pair of parallel lines that join the two carbons bonded by the  $\pi$  and the sigma bonds as shown by the following formulas:



Bond angles or positions of atoms in space are not shown by these formulas.

**Structure of Alkyne Molecules.** It can be shown by chemical reactions and by physical methods, such as spectroscopic methods, that any alkyne molecule contains a pair of carbon atoms that behave differently from any carbon atoms in alkane or alkene molecules. Let us consider the first member of the series, ethyne (acetylene,  $\text{C}_2\text{H}_2$ ), to see what is characteristic of the structure of alkyne molecules.

Ethyne molecules are linear; that is, all bond angles are  $180^\circ$ , as shown in Fig. 25-6a. It is thought that one of the  $s$  electrons in a carbon atom is promoted to an empty  $p$  orbital, and then the  $s$  orbital and one of the three  $p$  orbitals form two  $sp$  equivalent hybrid orbitals whose axes lies at  $180^\circ$  angles to each other. The two carbon and hydrogen atoms are then bonded by sigma bonds, as shown in Fig. 25-6a and b. However, the sigma bond is only a part of the bonding system joining the two carbon atoms.

Because only one  $p$  orbital was used to form the  $sp$  hybrid, each carbon atom possesses two ordinary  $p$  orbitals, each orbital containing

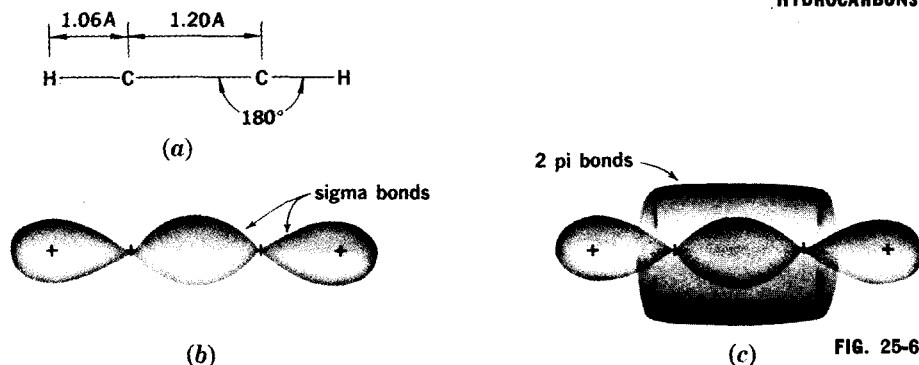
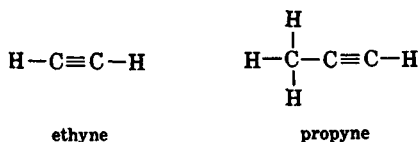


FIG. 25-6

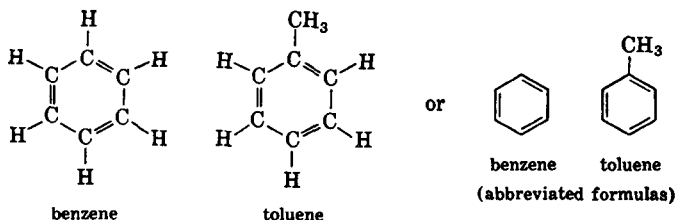
Schematic representation of an ethyne molecule: (a) positions in space of the carbon and hydrogen nuclei and bond angles; (b) sigma bonds between carbons and between hydrogen and carbon; (c) two pi bonds, formed by the lateral overlap of  $2p_y$  and  $2p_z$  orbitals, form a cylindrical electron cloud.

one electron. The carbon atoms are close enough to each other for the  $p$  orbitals to overlap laterally to form two pi bonds. Furthermore, the two pi bonds are thought to interact with each other to form an electron cloud that is cylindrically symmetrical around the line joining the two carbon nuclei, as shown in Fig. 25-6c.

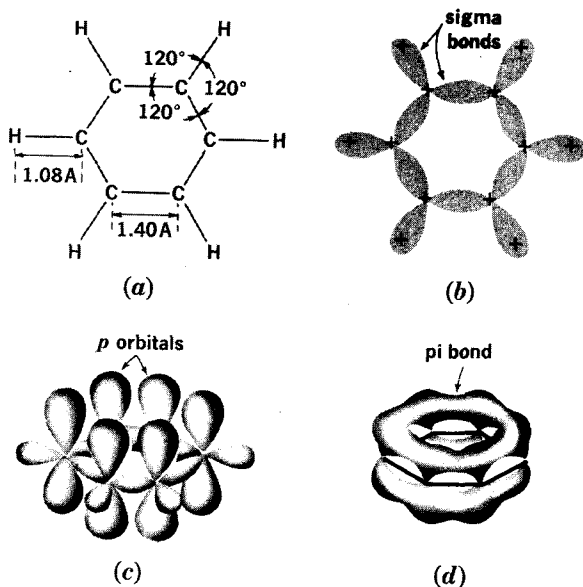
A simple representation of the structures of the alkyne molecules shows the three bonds (*triple bond*) with three parallel lines:



**Structure of Benzene Hydrocarbons.** Each benzene hydrocarbon molecule contains a group of six carbon atoms linked together in the form of a hexagonal ring and lying in a single plane. In benzene itself, a hydrogen atom is attached to each carbon atom. In toluene, the next member of the series, a hydrogen atom has been replaced by a methyl group. These ideas were first incorporated into structural formulas by the German chemist F. A. Kekulé in 1865. In order to allow for the tetravalence of carbon, he postulated alternate double and single bonds between the carbon atoms, as shown in the following formulas:







Schematic representation of a benzene molecule: (a) bond angles and positions in space of C and H nuclei; (b) sigma bonds involving  $sp^2$  and s orbitals; (c) p orbitals of C not involved in sigma bond formation (note that the plane of the benzene ring is now shown almost perpendicular to the plane of the paper); (d) the overlap of the p orbitals form the pi electron clouds above and below the benzene ring (centers of sigma bonds are indicated by the colored hexagon).

FIG. 25-7

Because of the presence of the three double bonds, the Kekulé formula suggests that benzene hydrocarbons have chemical properties very much like the alkene hydrocarbons. They do not. Also, the Kekulé formula suggests that the distances from carbon to carbon in the ring are alternately the distance between two adjacent carbon atoms in alkane molecules (1.54 Å) and the distance between two carbon atoms joined by a double bond in alkene molecules (1.34 Å). However, the distances, measured by X-ray diffraction, are uniform around the ring and are 1.39 Å. Today the benzene molecule is considered to be planar, with all carbon-carbon bonds the same length and all bond angles  $120^\circ$ , as shown in Fig. 25-7a.

The  $120^\circ$  bond angle indicates  $sp^2$  hybridization of the type described in alkene molecules. The bonds shown in Fig. 25-7b are sigma bonds, resulting from the overlap of an  $sp^2$  orbital of a carbon atom with an  $sp^2$  orbital of a second carbon or with an s orbital of hydrogen.

The fourth valence electron of carbon is not involved in  $sp^2$  hybridization and may be thought of for the moment as occupying a normal p orbital that lies above and below the plane containing the carbon nuclei (Fig. 25-7c). Because there are six carbon atoms in the ring, there are six of these orbitals, all parallel to one another and close enough for lateral overlap, that is, pi bond formation. However, each p orbital overlaps two neighboring p orbitals, one on either side, thus resulting in two doughnut-shaped electron clouds. One such doughnut lies above and one lies below the plane through the carbon nuclei (Fig. 25-7d). The participation of a single pi electron in the formation of more than one bond is called **electron delocalization**.

The structure of benzene molecules, as shown in Fig. 25-7, is in accord with the fact that benzene has a dipole moment of zero (Chap. 4). This structure is also in accord with the NMR spectrum of benzene (see Chap. 17).

Since the discovery of benzene by Michael Faraday in 1825, several graphic representations have been proposed. Some are



Kekulé  
1865



Claus  
1867



Dewar  
1867



Armstrong-  
Baeyer  
1887

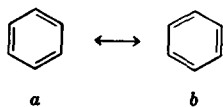


*a*

The graphic representation *a* has been proposed recently by several chemists and has had considerable acceptance. In this representation, the hexagon refers to that part of the benzene molecule shown in Fig. 25-7*a*, and the circle refers to the delocalized pi electrons shown in Fig. 25-7. Many chemists, especially organic chemists, continue to use the Kekulé representation. In this text, we shall use the circle formula unless it is important to center attention on specific bonds joining pairs of carbons, in which case we shall use the Kekulé formulas.

**RESONANCE STRUCTURES.** When it is possible to represent a molecule with two or more structural formulas that differ only in the placement of the valence bonds and not in the location of atomic nuclei, no single formula adequately represents the molecule. Rather, the actual structure is thought of as a *resonance hybrid* of the several inadequate formulas that may be written to represent it (see Chap. 17).

In the case of benzene, we can write two Kekulé formulas that differ only in the placement of single and double bonds:

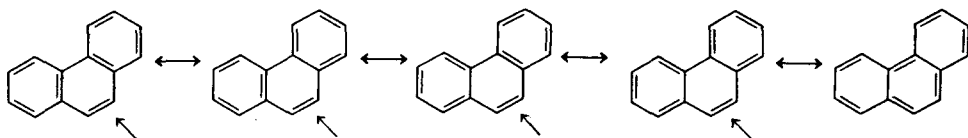


A double-headed arrow is used to show that the true structure of benzene partakes of both structures; that is, the real structure is a resonance hybrid of *a* and *b*. If any pair of carbon atoms in *a* is compared with the same pair in *b*, it is found that, if a single bond connects the pair in *a*, a double bond connects the same pair in *b*, or if a double bond connects the pair in *a*, a single bond connects them in *b*. This is taken to mean that all the bonds in the hybrid structure are alike and that they partake of both single and double bond character.

The student will recognize that for benzene the implications of the resonance hybrid representation and the hexagon—inner-circle representation (top of page) are the same. However, for more complicated structures, the resonance hybrid representation can give a better picture of the chemical properties of the molecule. To illustrate this,

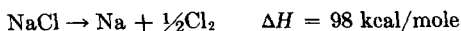
ORGANIC CHEMISTRY;  
HYDROCARBONS

consider the Kekulé formulas for phenanthrene, an aromatic hydrocarbon,  $C_{14}H_{10}$ , with three fused benzene rings:

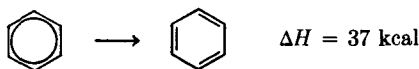


Only five Kekulé formulas can be written, and it is noteworthy that a double bond appears in four of these between the same pair of carbon atoms (marked  $\uparrow$ ). At no other position in the molecule does this happen. We might expect, therefore, the double bond joining these two carbon atoms to be more like an isolated ethene double bond than any of the others in phenanthrene, and we find this is true. This part of the phenanthrene molecule is very responsive to the addition reactions (see Chap. 26) that characterize the alkene hydrocarbons.

**RESONANCE ENERGY.** We have noted that exothermic compounds ( $\Delta H_f$  is negative) are relatively stable. For example, when 23 g of sodium and 35.5 g of  $Cl_2$  unite to form 58.5 g of NaCl, 98 kcal of energy is liberated. We can say that the sodium chloride is stabilized by this much energy, for we would have to supply this much energy in order to destroy the structure of sodium chloride and convert it into elemental chlorine and sodium:



In a similar way, we can say that the resonance hybrid structure of benzene is stabilized by 37 kcal of energy<sup>1</sup> as compared with a structure represented by a single Kekulé formula:



The energy required to change a mole of hybrid molecules to a mole of molecules having the structure shown by a single, conventional valence-bond formula is called its **resonance energy**. We shall have a number of occasions in the next chapter to refer to the added stability of molecules because of resonance energy, that is, because the molecules have less enthalpy or heat content than is predicted on the basis of a single conventional valence-bond formula. We might use the same kind of language in referring to an automobile in a ditch and say that it is stabilized by so much "ditch energy," meaning the amount of energy required to put it back on the road.

**SATURATED AND UNSATURATED HYDROCARBONS.** The carbon atoms in alkane molecules (and cycloalkanes to be discussed later in the chapter) are joined by single bonds only. Such hydrocarbons are

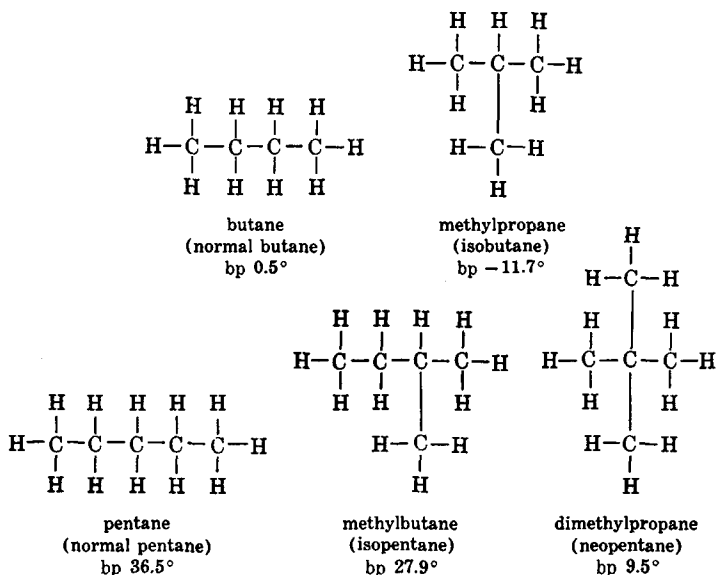
<sup>1</sup> The interested student is referred to a modern organic textbook for the method of measuring resonance energy.

called **saturated hydrocarbons**. On the other hand, at least one pair of carbon atoms in alkene, alkyne, and benzene hydrocarbon molecules are joined by multiple bonds, a condition represented in structural formulas with double and triple bonds for alkenes and alkynes, or with a circle inside a hexagon for benzene hydrocarbons. Hydrocarbons with one or more pairs of carbon atoms joined by multiple bonds are called **unsaturated hydrocarbons**.

## ISOMERISM

Compounds that have the same molecular formula but different structural formulas were defined in Chap. 19 as *isomers* (Greek *isos*, equal, and *meros*, part). The phenomenon is known as **isomerism**. Isomeric compounds are not possible among the alkanes till there are enough carbon atoms to permit more than one arrangement of the carbon chain. For each of the compounds  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_8$ , there is only one possible arrangement of the carbon chain. For  $\text{C}_4\text{H}_{10}$ , only two arrangements of the atoms are possible, and only two compounds with the formula  $\text{C}_4\text{H}_{10}$  have been discovered. For  $\text{C}_5\text{H}_{12}$  three arrangements are possible, and only three have been discovered. As the molecules become more complex, the numbers of isomers increase markedly (see Table 25-1).

Isomeric compounds differ both chemically and physically from one another. They can be identified experimentally by differences in melting point, boiling point, refractive index, and chemical activity. The structural formulas and boiling points for the two isomeric butanes and the three isomeric pentanes are as follows:

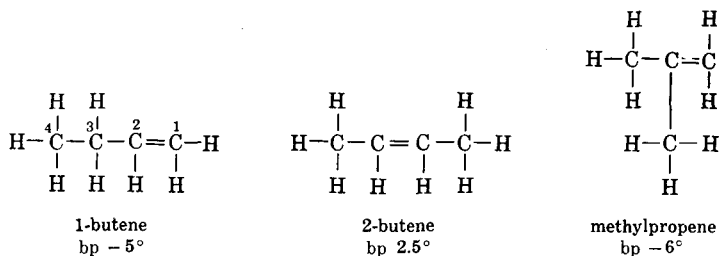


**ORGANIC CHEMISTRY;**  
**HYDROCARBONS**

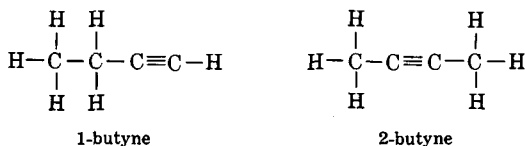
In the examples of isomerism just cited, the difference in structure arises from a different arrangement of the carbon atoms. That is, in normal butane, the four carbon atoms are joined in a continuous or unbranched chain, but in isobutane, three carbon atoms are in a continuous chain arrangement and the fourth carbon is joined to the middle carbon as a branch. Note that the isomer that has a continuous carbon chain without carbon branches is named as the normal isomer. The prefixes *iso*- and *neo*- are sometimes used to indicate branched-chain isomers.

There are many other ways by which isomeric compounds can result. For example, among the alkenes and alkynes, isomeric compounds can result when double and triple bonds occur at different places in the molecules. To illustrate this, let us consider the number of isomeric butenes,  $C_4H_8$ , theoretically possible.

If we use ball and stick models to represent possible molecules, we find that only three different alkene models can be constructed, and only three compounds with the composition  $C_4H_8$  and having the properties of alkenes are known. These three isomers have been shown to have the following structures (systematic naming of these compounds will be discussed in the next section):



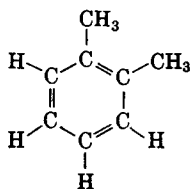
Again using balls and sticks, we find that we can construct only two model molecules that contain a triple bond and have the composition  $C_4H_6$  (butyne). Instead of three isomers, as was the case for the butenes,  $C_4H_8$ , only two isomeric butynes,  $C_4H_6$ , are predicted, and only two have ever been discovered. Their structural formulas are given below:



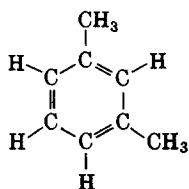
It is a fact of great importance that the number of isomers predicted by putting together models is precisely the number of isomers found by the most painstaking laboratory experimentations.

Isomeric compounds result if certain atoms or groups of atoms are attached at different locations in molecules. For example, four iso-

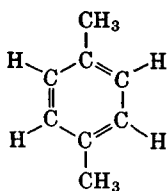
meric aromatic hydrocarbons are known that have the molecular formula  $C_8H_{10}$ :



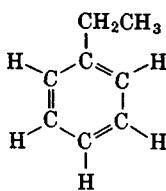
1,2-dimethylbenzene, or  
*ortho*-dimethylbenzene  
(*ortho*-xylene)



1,3-dimethylbenzene, or  
*meta*-dimethylbenzene  
(*meta*-xylene)



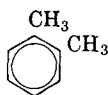
1,4-dimethylbenzene, or  
*para*-dimethylbenzene  
(*para*-xylene)



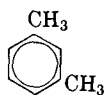
ethyl benzene

Other differences in structure that can give rise to isomerism are discussed in later chapters.

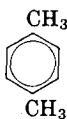
**ABBREVIATED STRUCTURAL FORMULAS.** The structural formulas written thus far for isomers are unnecessarily cumbersome and can be condensed, once we understand clearly what ideas they convey. For example, structural formulas for the four isomers of  $C_8H_{10}$  can be condensed to



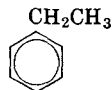
*ortho*-  
dimethylbenzene



*meta*-  
dimethylbenzene

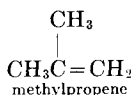
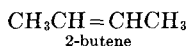
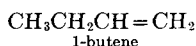


*para*-  
dimethylbenzene



ethylbenzene

The isomeric butenes shown on page 672 can be represented thus:



In order to save space, we shall frequently use condensed structural formulas, but the student should be able to translate these semi-structural formulas into more complete versions.

## SYSTEMATIC NOMENCLATURE

The systematic naming of a million-odd compounds is a vast problem indeed. Before the turn of the century the collection of known substances became so huge that a special international meeting, the Geneva Conference of 1892, was called to establish a systematic scheme of naming compounds. The rules of naming agreed on at this conference<sup>1</sup> are known as the Geneva System. One of the key rules establishes similar names for members of homologous series, for example, the alkanes.

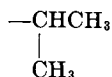
To complicate matters, however, the first few members of a given series have often been known for a long time and their names do not agree with the systematic names. These common names have become so firmly fixed in the chemical literature that it is virtually impossible to substitute their systematic names. Therefore, the student of organic chemistry finds it necessary to learn more than one name for each of the first few members of a given series.

The discussion of all the rules for systematic naming is beyond the scope of this book. Nevertheless, there are a few simple rules which are easily mastered and which enable one to name a great many compounds:

1. For the purpose of naming, a portion of the molecule is chosen that can serve as the **parent compound**. For alkanes, this portion is the longest continuous chain of carbon atoms; for alkenes and alkynes, it is usually the longest continuous chain containing the double or triple bond; for benzene hydrocarbons, it is usually the benzene ring.

2. For aliphatic hydrocarbons, the number of carbon atoms in the parent compound is denoted by the proper prefix, that is, meth-, eth-, prop-, but-, pent-, etc., for 1, 2, 3, 4, 5, etc., carbon atoms, respectively. The suffix -ane, -ene, or -yne is added to denote the hydrocarbon class. That is, if the longest chain of carbon atoms contains seven carbon atoms joined as a continuous chain and contains a double bond, the name of the parent compound is made by combining the prefix *hept-* for seven and the suffix *-ene* for the double bond, that is, *heptene*.

3. The chain or benzene ring of the parent is numbered with the lowest numbers possible to locate the positions where hydrogen atoms have been replaced by other atoms or groups of atoms (radicals), such as  $-\text{CH}_3$  (methyl),  $-\text{CH}_2\text{CH}_3$  (ethyl),  $-\text{CH}_2\text{CH}_2\text{CH}_3$  (normal propyl),



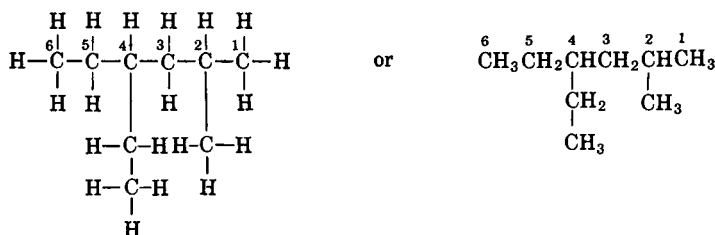
(isopropyl), etc. *Normal* and *iso* may be abbreviated *n-* and *i-*, respectively. The positions 1, 2-; 1, 3-; and 1, 4- in the benzene ring

<sup>1</sup> The rules have been kept up to date by later conferences sponsored by the International Union of Chemistry.

may also be designated by *ortho*, *meta*, and *para* (abbreviated *o*, *m*, and *p*), respectively.

4. The complete name of the compound is a combination of (a) the name of the parent portion, (b) the names of the attached radicals, and (c) the numbers that show where the radicals are attached. (These same rules may also be applied to the naming of certain compounds that are not hydrocarbons.)

Let us apply these rules to the naming of an isomer of nonane that has the structure shown below:

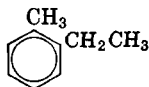
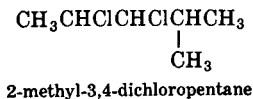
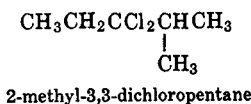


a. The longest continuous chain of carbon atoms contains six atoms, all joined by single bonds. This part is to be considered the parent hydrocarbon and is named *hexane* (*hex-* for six and *-ane* for single bonds).

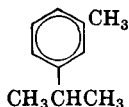
b. The hexane chain is numbered from right to left so as to locate with the lowest possible numbers the position where hydrogen atoms of the parent hydrocarbon have been replaced. These numbers, 2- and 4-, are used to designate the positions in the molecule of the  $-\text{CH}_3$  and  $-\text{CH}_2\text{CH}_3$  radicals. Note that, if the chain is numbered in the opposite direction, the numbers 3- and 5- would have to be used to locate these groups. Because we wish to use the lowest numbers possible in the name, we choose to number this chain from right to left.

c. The complete name is 2-methyl-4-ethylhexane.

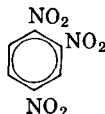
The structural formulas and names for several compounds, some of which are not hydrocarbons, follow. Study these to see how the names are derived from the rules that we have stated. The student is also advised to study the names given in earlier pages of this chapter in the light of these rules:



1-methyl-2-ethylbenzene,  
or  
*o*-methylethylbenzene



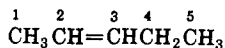
1-methyl-3-*i*-propylbenzene,  
or  
*m*-*i*-propylmethylbenzene



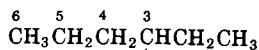
1,2,4-trinitrobenzene



Double and triple bonds are located by mentioning the lower of the numbers of the two carbon atoms joined by the multiple bond:



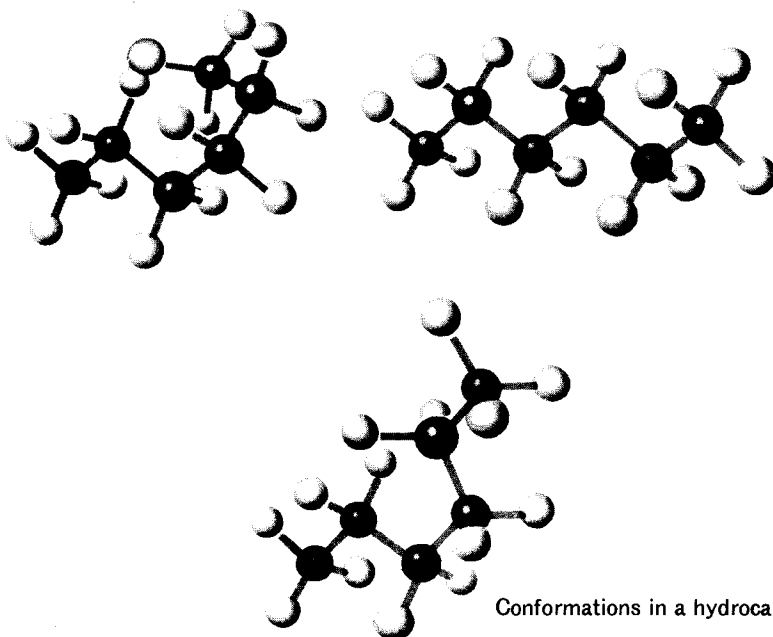
2-pentene



3-ethyl-1-hexyne

**Conformation of Molecules.** The condensed structural formulas that we write,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  for hexane, for example, do not give a proper representation of the groups in space. For one thing, the bond angles between carbon atoms are  $109^\circ 28'$  instead of  $180^\circ$ , so that the carbon atoms do not lie on the same line as indicated. Also, groups such as  $\text{CH}_3\text{CH}_2-$  and  $\text{CH}_3\text{CH}_2\text{CH}_2-$  may assume different positions in space because of rotation about the  $sp^3$  bond. These two factors allow the carbon chain to be folded in a variety of ways, a few of which are shown in Fig. 25-8. The various positions in space that a hydrocarbon molecule can take because of rotation about  $-\text{C}-\text{C}-$  bonds are referred to as **conformations**.

As can be seen in Fig. 25-8, certain conformations represent a crowded condition for some of the atoms not bonded to one another



Conformations in a hydrocarbon molecule.

FIG. 25-8

and result in increased repulsions between them. Hence, we might expect certain conformations to be less stable than others and less likely to represent the true shapes of the majority of the molecules.

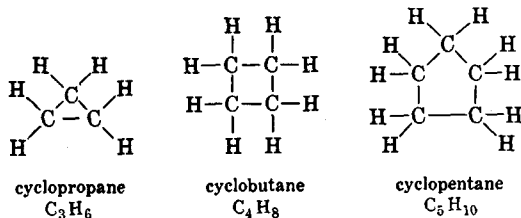
## SOURCES OF ALKANE HYDROCARBONS

The alkane hydrocarbons are found chiefly in natural gas and petroleum. The alkenes and alkynes do not occur abundantly in nature. They are obtained by *cracking* and other processes that are discussed later.

**Natural Gas.** Natural gas is often encountered in drilling wells for petroleum. The important producing areas in the United States are Pennsylvania, West Virginia, Louisiana, Texas, Oklahoma, Kansas, Indiana, Ohio, Kentucky, and California. Natural gas is made up of about 50 to 94 per cent methane. Some ethane, propane, and other paraffin hydrocarbons of low molecular weight are also present. Natural gas is thought to have originated as petroleum did, that is, from plant and animal materials. About 12 trillion ft<sup>3</sup> are used annually in the United States, mostly for fuel, both domestic and industrial.

**Petroleum.** Petroleum is a complex liquid solution of gaseous, liquid, and solid hydrocarbons. Also present are small amounts of nitrogen and sulfur compounds. The low-distilling hydrocarbons that make up petroleum ether, gasoline, and kerosene belong mostly to the methane series. The crude oil remaining after the volatile hydrocarbons have been removed may be composed mainly of alkanes (paraffin base) or of cycloparaffins (asphalt base), both with high molecular weights.

The cycloparaffins are members of a homologous series of saturated cyclic hydrocarbons, isomeric with the alkenes ( $C_nH_{2n}$ ). The extra pair of electrons is utilized in joining the ends of the carbon chain into a ring, rather than in forming a double bond. The first three members are



Cyclopropane and cyclobutane are unstable compounds, probably because the bond angles necessary for ring formation ( $60^\circ$  and  $90^\circ$ , respectively) are too different from the tetrahedral angles characteristic of the alkanes and cycloalkanes. As the number of carbon atoms increase, the rings can pucker or fold so as to give bond angles of about  $109^\circ 28'$  (Fig. 25-9).

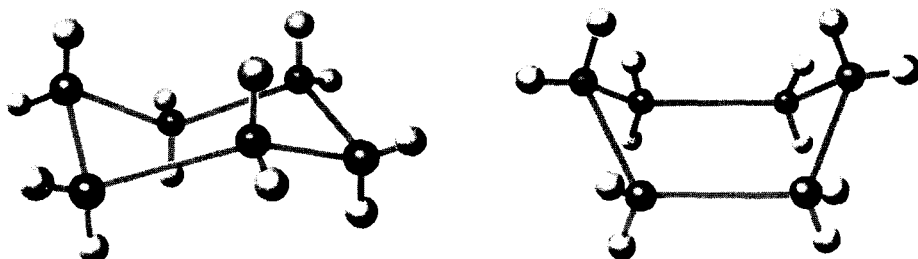


FIG. 25-9

Ball-and-stick models for two conformations of cyclohexane show how the tetrahedral angle between carbons is achieved by puckering of the rings.

Of the total annual petroleum production—about 7,000,000,000 barrels—the United States produces about 37 per cent. The energy derived from the combustion of this amount of petroleum is estimated to be equivalent to the work done in one year by about 13 billion men, working a 40-hour week.

**REFINING OF PETROLEUM.** The first step in refining petroleum consists of separating petroleum by **fractional distillation** into batches with different boiling ranges (Table 25-2). Crude oil is pumped continuously through a furnace, where it is heated. The hot liquid then passes into a “flash chamber,” where, by lowering the pressure, the lower-boiling components are vaporized. The vapors pass into a “bubble tower” (see Fig. 25-10). Here the higher-boiling components are condensed in the lower portion of the tower and flow downward

TABLE 25-2 *Hydrocarbon fractions obtained from petroleum*

fraction	size range of molecules	boiling-point range, °C	uses
gas	C <sub>1</sub> -C <sub>5</sub>	-164-30	gaseous fuel; production of carbon black, hydrogen, or gasoline (by polymerization)
petroleum ether (ligroin)	C <sub>5</sub> -C <sub>7</sub>	30-90	solvent; dry cleaning
gasoline (straight-run)	C <sub>5</sub> -C <sub>12</sub>	30-200	motor fuel
kerosene	C <sub>12</sub> -C <sub>16</sub>	175-275	illuminant; fuel
gas oil, fuel oil, and diesel oil	C <sub>15</sub> -C <sub>18</sub>	250-400	furnace fuel; fuel for diesel engines; cracking
lubricating oils, greases, petroleum jelly	C <sub>16</sub> up	350 up	lubrication
paraffin (wax)	C <sub>20</sub> up	melts 52-57	candles; waterproofing fabrics; matches; home canning
pitch and tar		residue	artificial asphalt
petroleum coke		residue	fuel; electrodes

from plate to plate. The ascending vapors bubble through the liquids that have condensed in the plates; hence the more volatile lower-boiling components collect in the upper portion of the tower. Distilla-

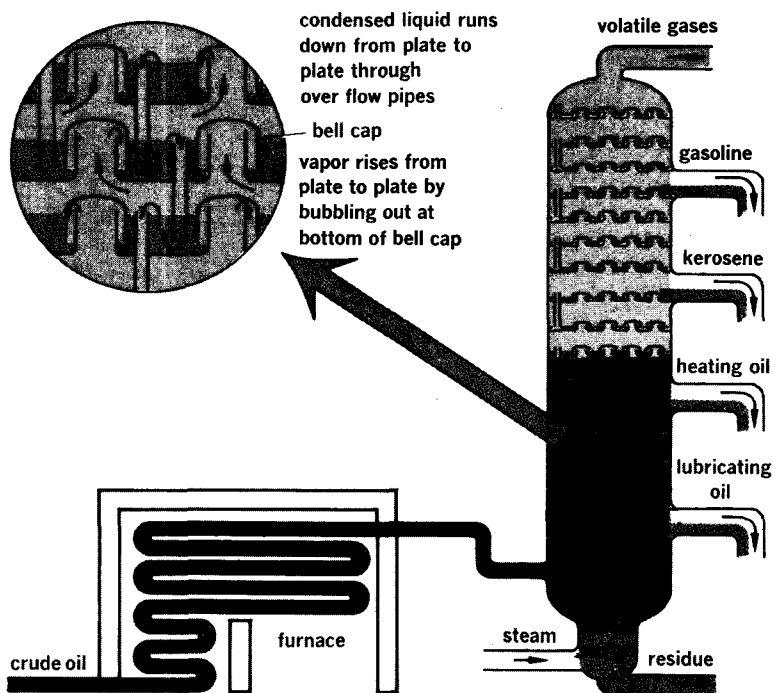


FIG. 25-10

Diagram of a fractionating tower for petroleum distillation. The cutaway view shows how the vapor and liquid phases are kept in contact with each other so that condensation and distillation occur all up and down the column.

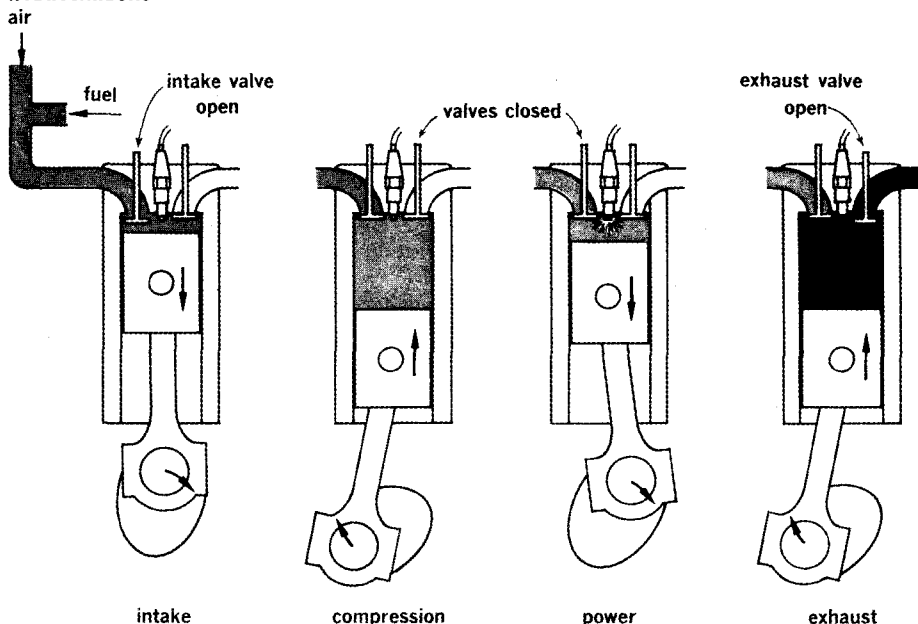
tion carried out in this manner affords an excellent separation into portions called **fractions**. Each fraction consists of a mixture of compounds, boils in a certain range of temperature, and is of rather definite composition. Practically speaking, each plate represents a separate distilling unit, and the whole process amounts to several distillations.

## GASOLINE

Prior to 1910, kerosene was the most valuable component of petroleum because of its use in lamps as an illuminant. With the advent of the automobile and electric lights, kerosene as such was relegated to a minor position, and gasoline assumed the major role. The hydrocarbons in gasoline have boiling points sufficiently low so that gasoline changes into a vapor in the gasoline engine.

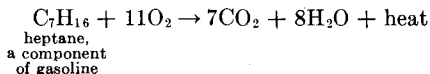
In the operation of a gasoline engine, the downstroke of the piston draws a mixture of gasoline vapor and air into the cylinder. This

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**FIG. 25-11** A schematic representation of how the chemical energy of gasoline and oxygen is converted into the kinetic energy of a running automobile engine.

mixture is compressed into a small volume at the top of the cylinder by the upstroke. When the piston nears the top of the upstroke, the timing system produces a spark across the spark plug gap that ignites the gasoline (Fig. 25-11). The burning of the gasoline may be represented as follows:



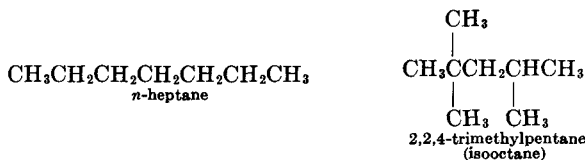
Small amounts of carbon and carbon monoxide are formed by incomplete combustion. The hot expanding gases push the piston down, thus turning the crank shaft. Only about 10 per cent of the chemical energy originally present in the fuel is converted into useful work; the remainder is dissipated largely as heat energy.

For the engine to run smoothly, burning must start at the proper time at the spark plug and move through the gas mixture at a fast, uniform rate. For straight-run gasoline, the rate of burning tends to be uniform till perhaps three-fourths of the gasoline is consumed; then the rate suddenly accelerates up to four times the original. This causes knocking, decreases power, and increases wear on the engine.

High-compression engines, in which there is less space at the top of the cylinder so that the upstroke of the piston puts the fuel mixture under a higher pressure, give more power and more efficient operation. Unfortunately, however, as the compression ratio goes up, the ten-

dency to knock also increases. Hence low-compression engines had to be used until gasoline could be produced that had good anti-knock properties.

**OCTANE NUMBER.** A large percentage of the molecules in straight-run gasoline are of the unbranched-chain variety, the type of hydrocarbon that produces knocking. Hydrocarbons whose molecules are of the branched-chain variety have antiknock characteristics. As a means of measuring the knocking properties of gasoline, two pure hydrocarbons were selected to be used as standards. One, *n*-heptane, is of the unbranched-chain type; the other, 2,2,4-trimethylpentane (isooctane), is of the branched-chain type.



They were assigned octane numbers of 0 and 100, respectively. When a gasoline is being rated, various mixtures of the two standard hydrocarbons are tried in a test engine till a mixture is found that produces the same knocking as the gasoline being rated. The percentage of isooctane in the standard mixture is then taken as the octane number of the gasoline being rated. For example, a 70-octane gasoline gives the same knocking in a test engine as a mixture containing 30 per cent *n*-heptane and 70 per cent isooctane. Note that whether the gasoline being rated actually contains any *n*-heptane and isooctane is not determined.

**High-octane Gasoline.** The high-octane gasoline on the market today is made in several ways.

Lead tetraethyl,  $\text{Pb}(\text{C}_2\text{H}_5)_4$ , when added to gasoline in concentrations up to 0.01 per cent, inhibits knocking. Approximately 85 per cent of all gasoline now sold in the United States contains either lead tetraethyl or similar lead alkanes.

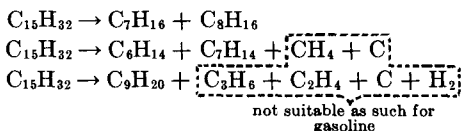
Gasolines produced by *cracking*, *polymerization*, *isomerization*, and *aromatization* are made up largely of aliphatic branched-chain hydrocarbons or of aromatic hydrocarbons. They are high-octane gasolines. By properly blending them with straight-run gasoline and adding lead tetraethyl, *premium gasolines* with octane ratings of about 100 have been made available.

**THERMAL CRACKING.** The hydrocarbons with high molecular weight that are present in gas oil and kerosene are unsatisfactory as a fuel for the usual automobile engine because of their high boiling points. The process by which these larger hydrocarbon molecules are broken down into smaller, more volatile molecules by heating is called **cracking**.

Not only does cracking increase the amount of gasoline obtained from petroleum, but the gasoline is of a superior quality.

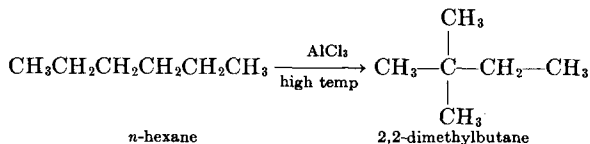
A wide variety of cracking processes are used in the United States. In general, the material to be broken down is fed through the cracking chambers in a continuous stream at temperatures and pressures ranging, respectively, from 400 to 600°C and from 10 to 250 psi. The catalysts (natural clays or alumina-silica mixtures) used in the more modern processes are in the form of a powder so fine that it can be transported through the chambers like a gas stream. This permits continuous operation and an output of hundreds of thousands of gallons of high-octane gasoline daily with a minimum amount of labor.

The cracking process also produces a certain amount of substances that are not suitable for gasoline stock. The following equations illustrate some of the possible products:



The unsaturated hydrocarbons, such as ethene and propene, are used in a variety of ways in chemical synthesis, as in the production of alcohol, synthetic rubber, etc.

**ISOMERIZATION (REFORMING).** The octane number of straight-run gasoline (50 to 55) can be increased by putting the gasoline through a cracking operation in which the catalyst is aluminum chloride or aluminum bromide. In this process, which is called **isomerization**, unbranched-chain hydrocarbons are converted into isomeric branched-chain hydrocarbons. The latter may have octane numbers above 100:



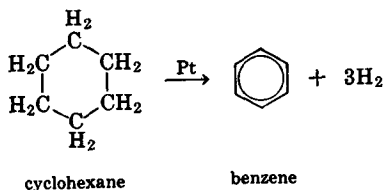
**POLYMERIZATION AND ALKYLATION.** More than 300 billion ft<sup>3</sup> of methane, ethene, ethane, propene, propane, and the butenes and butanes is produced annually in the United States as by-products in the cracking process. These hydrocarbons cannot be used as such in gasoline because of their low boiling points. However, processes have been developed recently whereby the small molecules can be made to recombine and form larger molecules like those in gasoline. The process in which similar molecules combine and form larger molecules is called **polymerization**, and the resultant molecules are called **polymers**.

**Sources of Aromatic Compounds. COAL.** Coal has long been an indirect source of many aromatic compounds. On destructively distilling

coal to produce coke, some of the coal is converted into a black, viscous liquid called *coal tar*. This tarlike liquid is separated into pure compounds by fractional distillation, together with crystallization processes, centrifuging, and solvent extraction. One ton of coal yields about 140 lb of tar, along with about 1,500 lb of coke, 10,000 ft<sup>3</sup> of coal gas (mostly hydrogen and methane), and about 25 lb of ammonium salts. The 140 lb of coal tar in turn produces from about 8 to 15 lb of phenol and cresols, 14 to 18 lb of naphthalene, 1 lb of benzene, 3 lb of toluene and the xylenes, small amounts of many other aromatic compounds, and about 70 lb of pitch.

**PETROLEUM.** The amount of benzene that can be produced yearly from coal tar depends on the supply of coal tar, which, as was said above, is a by-product in the coke industry. Coke is used in the production of iron and steel, which means that the supply of coal tar is subject to the ups and downs of industry as a whole. On the other hand, the demand for benzene and its derivatives has increased steadily till today the annual consumption is around 350 million gal. Most of this goes into the production of aniline (dyes, drugs), phenol (dyes, drugs, and plastics), styrene (synthetic rubber), intermediates for the production of insecticides, nylon, and synthetic detergents. Because the demand has exceeded the supply of by-product benzene and because a short supply means a rise in price, it is now profitable to produce benzene and other aromatic compounds from petroleum products.

In one process recently developed by one of the major oil companies, straight-run gasoline (825,000 barrels per month) is fed into huge distilling columns to separate such cyclic hydrocarbons as cyclohexane, methylcyclopentane, and methylcyclohexane from the gasoline. The stream containing these cyclic compounds is then fed into the "reformer" towers, where these compounds are catalytically converted into benzene and toluene with the liberation of hydrogen. Platinum is employed as the catalyst, and the reaction is carried out at a moderately high temperature and pressure. The following equation shows the type of change that occurs:



This type of chemical change is called **aromatization**. Huge amounts of benzene and toluene are also made from the aliphatic hydrocarbons in a reaction involving ring closure and dehydrogenation (aromatization).



## CHAPTER REVIEW

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### *Terms*

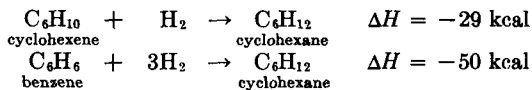
Organic and inorganic compounds, vital force, alkanes, alkenes, alkynes, benzene hydrocarbons, aromatic, aliphatic, paraffins, homologous series, homolog,  $sp^3$  bond, tetrahedral structure, structural formula,  $sp^2$  bond, sigma bond, pi bond, double bond,  $sp$  bond, triple bond, benzene ring, electron delocalization, resonance hybrid, Kekulé formula, resonance energy, isomerism and isomers, *o*-, *m*-, and *p*-isomers, condensed structural formula, parent compound, systematic naming, conformation of molecules, fractional distillation, octane number, cracking, polymerization, isomerization, aromatization.

### *Exercises*

1. Can you suggest a test that one might use to determine if a newly discovered compound is organic or inorganic?
2. What discoveries aided in discrediting the vital-force theory? Over what period of time did this occur, and what was the effect on the development of the field of organic chemistry?
3. Write the molecular formula of a homolog of the alkane series containing 25 carbon atoms; of a homolog of the alkyne series containing 25 carbon atoms.
4. Would a homologous series of hydrocarbons probably exist in which each member differs from a preceding member by one carbon and three hydrogen atoms? Explain.
5. Why is it necessary to postulate  $sp^3$  hybridization for the four carbon bonds in methane,  $CH_4$ ?
6. Show with sketches similar to Fig. 25-2 the sigma bonds in the two isomeric butanes,  $C_4H_{10}$ .
7. Why is it necessary to show a different kind of bond hybridization for ethene molecules from that used for ethane molecules?
8. Distinguish between sigma and pi bonds.
9. Show with a sketch similar to Figs. 25-2 and 25-5 the bonding orbitals in propene,  $C_3H_6$ .
10. Describe the bonding orbitals present in butyne,  $C_4H_6$ .
11. What is a simple way of showing in structural formulas that two carbon atoms are joined by one sigma and one pi bond; by one sigma and two pi bonds?
12. What is meant by electron delocalization?
13. Write all possible Kekulé formulas for naphthalene,  $C_{10}H_8$ . We can say that naphthalene is a resonance hybrid of how many Kekulé structures?
14. Write structural formulas for all the isomers of  $C_6H_{12}$ . Name each isomer.
15. Write a structural formula for 2-hexene; for 3-ethyl-1-heptyne.
16. Write condensed structural formulas for the compounds mentioned in Exercises 14 and 15.

17. Write condensed structural formulas for all the benzene hydrocarbons with a molecular formula,  $C_9H_{12}$ . Name each.
18. What is meant by conformation of molecules?
19. On the basis of the balanced equation for the complete combustion of octane, calculate the weights of carbon dioxide and of water formed per gallon of gasoline used in a car. The density of gasoline is 0.69 g/ml.
20. How is octane rating of gasoline defined?
21. How does the structure of hydrocarbon molecules in straight-run gasoline differ from that in high-octane gasoline?
22. Show with equation how an aliphatic hydrocarbon might be converted to an aromatic hydrocarbon. Show how an aromatic hydrocarbon might be converted to an aliphatic hydrocarbon.
23. Calculate the resonance energy of benzene from the heats of hydrogenation

tion of cyclohexene, , and benzene:



Hint: First calculate what the heat of hydrogenation of benzene should be if each molecule actually contained three double bonds of the cyclohexene type.

24. One type of distilling column can be packed with glass beads, or it can be left unpacked during a distillation. Which, packed or unpacked, would result in a better separation of two liquids by distillation, one liquid having a vapor pressure of 560 mm at 85°C, and the other 200 mm at the same temperature.

## SUPPLEMENTARY READING

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# PROPERTIES OF

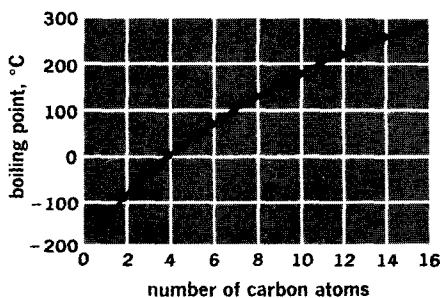
## HYDROCARBONS; HALOGEN

### DERIVATIVES

#### PHYSICAL PROPERTIES



The alkanes, alkenes, alkynes, and benzene hydrocarbons are very much alike physically. All are colorless compounds, insoluble or only slightly soluble in water, but quite soluble in nonpolar solvents. The hydrocarbons with low molecular weights,  $C_1$  to about  $C_6$ , are gases; those with intermediate weights are liquids; and those with high molecular weights are solids (compare Table 25-2). The actual melting and boiling points vary for molecules with the same number of carbon atoms, depending on the presence or absence of double and triple bonds and the number and



Boiling points of the first 15 normal alkanes.

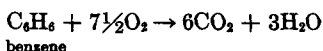
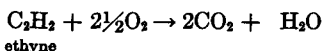
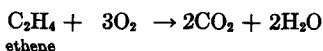
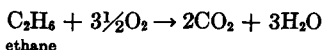
FIG. 26-1

kind of chain branches. For the unbranched-chain members of a given aliphatic series, the melting and boiling points increase fairly regularly as the molecular weight increases (Fig. 26-1). The boiling points of the branched-chain hydrocarbons are generally lower than

those of their unbranched isomers. The melting and boiling points of benzene hydrocarbons are usually higher than the aliphatic hydrocarbons with the same number of carbon atoms; for example, the boiling points of hexane, 1-hexene, 1-hexyne, and benzene are 69, 64, 72 and 80°C, respectively.

## CHEMICAL PROPERTIES

**Combustion.** All hydrocarbons have one important chemical property in common. They are all combustible, burning in oxygen or air to carbon dioxide and water.



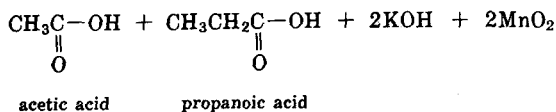
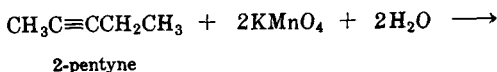
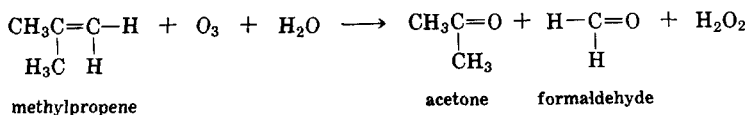
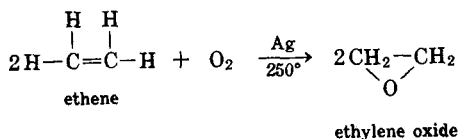
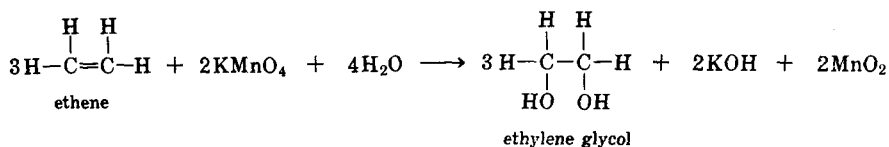
The combustion of hydrocarbons in a gasoline engine, a diesel engine, an oil furnace, or a gas stove does not take place so completely as the above equations imply. Some carbon monoxide, carbon (soot), and even hydrocarbons may constitute an appreciable fraction of the combustion products, depending on how the combustion is carried out. When natural gas, consisting mainly of methane with some ethane and propane, is burned in a laboratory burner or a gas stove, the ratio of air to gas and the mixing of the two can be controlled so as to give very little carbon monoxide, carbon, and other undesired combustion products. On the other hand, when diesel fuel ( $\text{C}_{14}\text{H}_{30}$ ,  $\text{C}_{15}\text{H}_{32}$ , etc.) is injected into the combustion chamber as a spray, the mixing with air is not nearly so good, and the combustion products contain an undesirable amount of unburned products. The same is true, usually to a lesser extent, of combustion of gasoline in an automobile engine.

**CONTROLLED OXIDATION.** The cheapest and most widely used oxidizing agent is atmospheric oxygen. But, as we have just seen, oxidation of hydrocarbons with atmospheric oxygen tends to take place readily only at temperatures above the kindling temperature of the hydrocarbon; at these high temperatures combustion results in the formation of carbon dioxide and water and the liberation of a maximum amount of heat energy. This, of course, is desirable if we are interested in liberating energy for useful work or heat. But if we are interested in producing chemicals from hydrocarbons by partial and selective oxidations of organic molecules, special procedures must be employed to control the oxidations so that products other than carbon dioxide and water form. Often, low-temperature oxidizing agents,

**PROPERTIES OF HYDROCARBONS;  
HALOGEN DERIVATIVES**

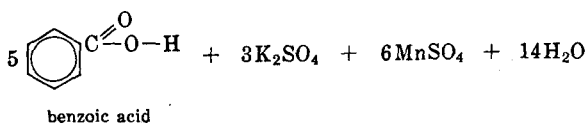
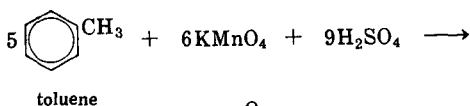
such as ozone, hydrogen peroxide, and potassium permanganate, are used; in some commercial processes, relatively low-temperature oxidation with atmospheric oxygen can be carried out in the presence of a catalyst.

The alkane hydrocarbons are inactive at normal temperature toward common oxidizing agents. On the other hand, the alkenes and alkynes react readily, the double or triple bond being the reactive point in the molecule. Examples:

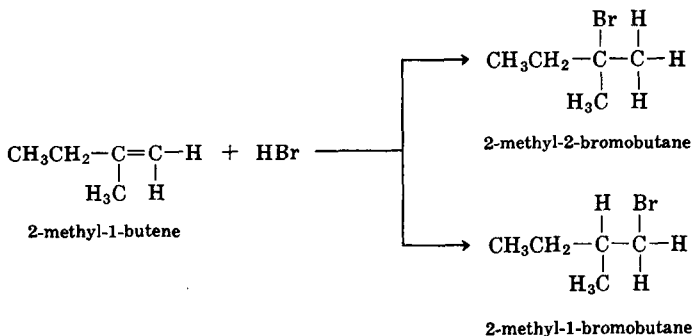
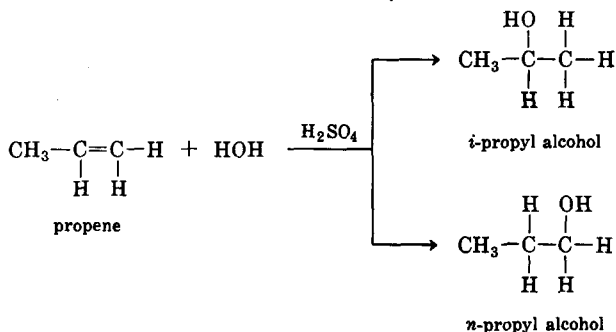
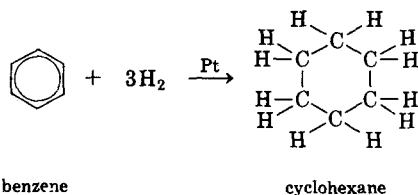
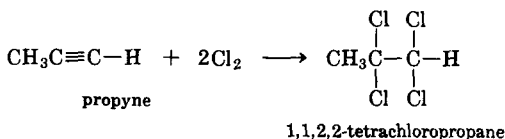
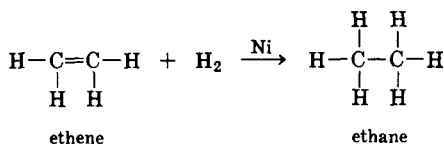


Alkadienes and alkatrienes (two and three double bonds in the carbon chain) tend to undergo slow oxidation in the air at ordinary temperatures to form gums and waxes. For this reason, their presence in gasoline and lubricating oils is undesirable. The drying of oil paints is due to air oxidation of alkadiene and -triene carbon chains in linseed oil, tung oil, etc. This oxidation produces the tough, water-insoluble film of the painted surface.

Carbon chains attached to a benzene ring are easily oxidized to acid groups:



**Addition Reactions.** In alkenes, alkynes, and benzene hydrocarbons, two or more carbon atoms are joined by both sigma and pi bonds. Under the proper conditions, atoms or groups of atoms react with these carbons by *addition*. During the addition, pi bonds change to  $sp^3$  orbitals and then form sigma bonds with the atoms being added to the molecule. The net result is that addition occurs without cleavage of the sigma bond between the pair of carbon atoms. Reactions of this type are called **addition reactions**. Examples are:



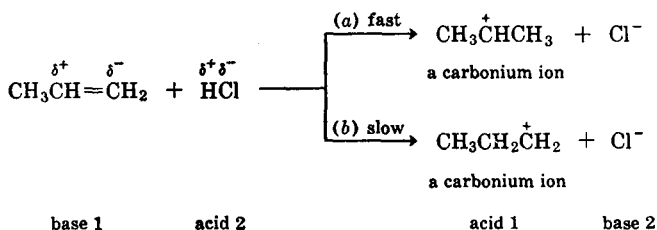
PROPERTIES OF HYDROCARBONS;  
HALOGEN DERIVATIVES

The first and third of the foregoing reactions are examples of *hydrogenation* reactions, that is, the addition of hydrogen to a multiple bond.

**MARKOWNIKOFF'S RULE.** Each of the last two additions just written results in the formation of two isomers; the isomer shown first in each case represents the major portion of the product. One can usually predict which isomer will form in the larger amount by a rule formulated by the Russian V. V. Markownikoff in 1869: *When HX adds to an unsymmetrical alkene, X tends to join the carbon atom having the fewer number of H atoms, and H joins the carbon atom already having the larger number of H atoms.*

**Mechanism of Addition Reactions.** Most organic reactions are thought to proceed in a stepwise fashion. It is of considerable interest to the research chemist to work out the nature of the different steps of a reaction, that is, the **mechanism of a reaction**.

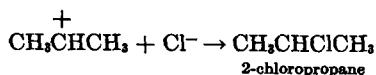
According to the commonly accepted view, alkenes and alkynes, because of the availability of their pi electrons, act as electron-pair donors, that is, Lewis bases (see page 329), and protons from addition reactants, such as HCl, HBr, and HOH, act as Lewis acids, that is, electron-pair acceptors. The first step, then, of the addition of HX to an alkene is the addition of a proton, that is, a Lewis acid-base reaction. Let us illustrate with the addition of HCl to propene. Because this is an unsymmetrical alkene, the addition may proceed two ways:



For (a), the two pi electrons originally associated with the double bond are now held between the end carbon and the added proton as a covalent bond; the middle carbon, now deficient in an electron, is left with a + charge. For (b), the proton has added to the middle carbon atom, leaving the end carbon with a + charge.

The addition of a proton to the carbon, of course, results in the formation of a positive ion. Such ions are called **carbonium ions**. It has been shown that the stability of carbonium ions increases as the number of H atoms bonded to the carbon bearing the plus charge decreases; for example,  $\text{CH}_3\overset{+}{\text{C}}\text{H}_2$  is less stable than  $(\text{CH}_3)_2\overset{+}{\text{C}}\text{H}$ , which is less stable than  $(\text{CH}_3)_3\overset{+}{\text{C}}$ . For this reason, in the addition of HCl to propene, the more stable carbonium ion  $\text{CH}_3\overset{+}{\text{C}}\text{HCH}_3$  tends to form in a greater amount than the less stable  $\text{CH}_3\text{CH}_2\overset{+}{\text{C}}\text{H}_2$ .

The second step of the addition is again a Lewis acid-base reaction, with the carbonium ion acting as the Lewis acid and the  $:\ddot{\text{Cl}}:^-$  ion as the electron pair donor:

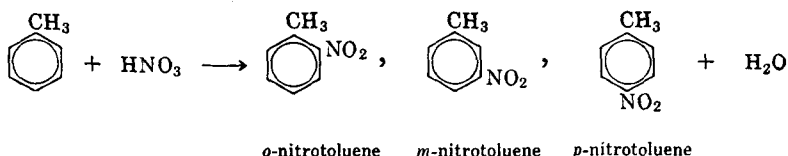


Chemicals that act as Lewis acids are often referred to as **electrophilic reagents** (electron-loving). The corresponding term for reagents that act as Lewis bases is **nucleophilic reagents** (nucleus-loving).

## TRANSITION STATE

We saw in Chap. 12 that many reactions proceed slowly at a given temperature, because only a few molecules have the high energy (activation energy) necessary to make and break bonds. For the reaction that we have been discussing, the addition of hydrogen chloride to propene, not all collisions of high-energy molecules result in a reaction. For example, a collision of a hydrogen chloride and an ethene molecule would be fruitless if the molecules were improperly oriented at the time of the collision—such as the Cl end of HCl being turned toward the ethene molecule at the moment of impact. Also, fruitless collisions may occur between high-energy molecules properly oriented, if the excess energy is located at the wrong place in the molecule. If the excess energy is associated with vibrations that stretch the H—Cl bond, the addition will be facilitated; if associated with the vibrations of a C—H group in  $-\text{CH}_3$ , the addition will not be facilitated.

The condition of colliding, energetic molecules that is necessary for a reaction to occur is called the **transition state**. This is the state that exists at the instant of potentially efficient collision: the two colliding molecules are oriented properly, and the bonds to be broken have been stretched to the required distance. The transition-state process is shown schematically in Fig. 26-2. Although we may not be able to picture a transition state accurately, the recognition that a preferred condition must exist for the reaction to occur and the consideration of the activation energy that must be available to attain this condition help us understand why certain reactions follow a particular course. For example, when toluene is nitrated three isomeric nitrotoluenes are formed:



However, mainly *o*- and *p*-nitrotoluene are formed; very little *m*-nitrotoluene is formed. Why? Transition states contribute to our



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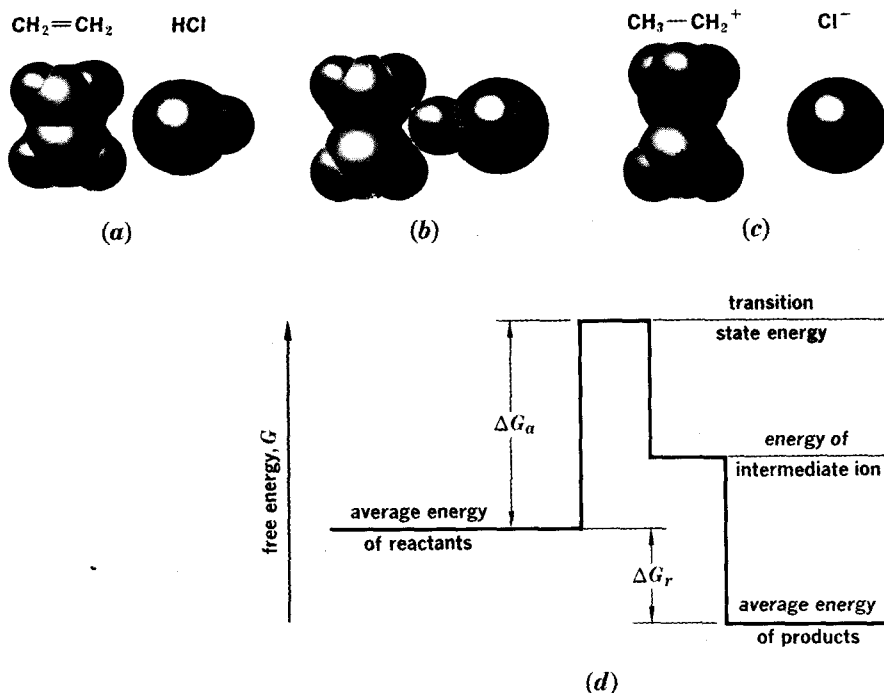


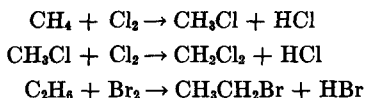
FIG. 26-2

The transition state: (a) two molecules collide and bounce away without reacting; (b) two molecules with the requisite activation energy and orientation are in the act of colliding; this condition represents the transition state; (c) a carbonium ion and a chloride ion separate; (d) a schematic representation for the free energy changes  $\Delta G_a$ , free energy of activation, and  $\Delta G_r$ , the overall free energy change for the addition.

understanding of this and similar problems (see "Directive Influences of Groups Attached to the Benzene Ring").

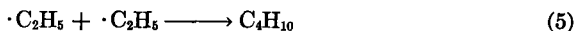
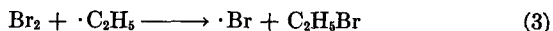
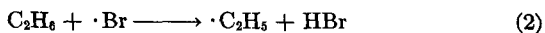
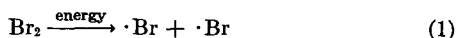
**Substitution Reactions of Alkanes.** The alkanes are inactive toward common laboratory reagents, such as acids, bases, and oxidizing agents, unless the temperature is unusually high. And they do not participate in addition reactions; they are *saturated compounds*.

At elevated temperatures or in the presence of ultraviolet light, one or more hydrogen atoms in an alkane molecule may be replaced by atoms of chlorine, bromine, or other similar groups:



The substitution of halogen for hydrogen in alkane molecules is thought to proceed by a *free-radical* mechanism. A *radical* is an atom or group of atoms with an unpaired electron.

In the first step of the bromination of ethane, high temperature or light furnishes energy for dissociating bromine molecules into free radicals (atoms in this case), as shown in Eq. (1). Radicals are extremely reactive and usually exist at normal temperatures for only a fraction of a second:



before colliding with other atoms to form covalent bonds. The collision most likely to occur is with another bromine molecule (which would produce no overall change), or with an ethane molecule, Eq. (2), to form an ethyl radical and a molecule of hydrogen bromide. Collision of an ethyl radical with a bromine molecule produces the desired compound,  $\text{C}_2\text{H}_5\text{Br}$ , and another bromine atom, Eq. (3), so that the whole chain of events may be repeated. The energy released by the formation of the C—Br and the H—Br bonds is greater than that needed to break the Br—Br and the C—H bonds so that the overall reaction is exothermic.

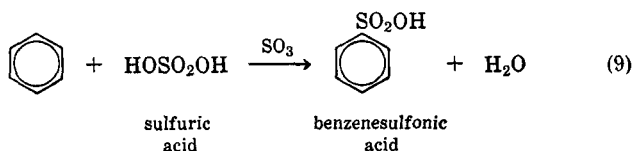
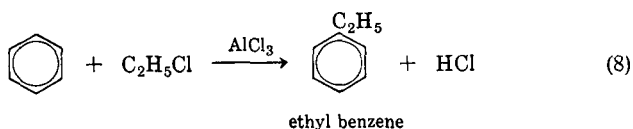
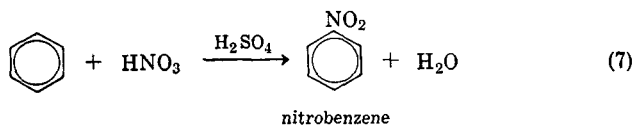
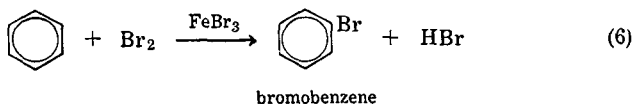
The sequence of reactions shown by Eqs. (1), (2), and (3) is called a *chain reaction*. Chain breaking reactions, Eqs. (4) and (5), take place slowly because of the low concentration of free radicals as compared with the concentration of molecules; that is, it is much more likely that a radical, once formed, will collide with a molecule rather than with another radical.

As the reaction proceeds and the concentration of  $\text{C}_2\text{H}_5\text{Br}$  increases, molecules of  $\text{C}_2\text{H}_5\text{Br}$  collide with  $\cdot\text{Br}$  radicals, and  $\text{C}_2\text{H}_4\text{Br}_2$  forms. And  $\text{C}_2\text{H}_4\text{Br}_2$  in the reaction mixture can lead to  $\text{C}_2\text{H}_3\text{Br}_3$ , etc. As is the case here, and with a great number of organic reactions, the reaction proceeds so that several competing reactions develop, and the reaction product consists of a variety of compounds. Often when the research organic chemist sets out to prepare a certain organic compound, he must reconcile himself to the tedious job of separating several similar compounds from the reaction mixture and be content with a yield of the desired pure compound ranging from a low percentage to perhaps 50 or 60 per cent.

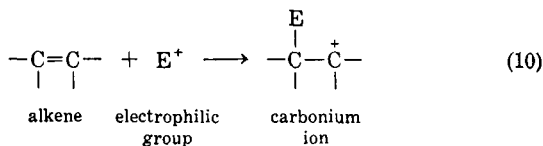
**Aromatic Substitution.** Although benzene and its homologs do undergo some of the addition reactions characteristic of the alkene and alkyne hydrocarbons, usually more drastic conditions, such as increased concentrations, higher temperatures, and different catalysts, are required to make the additions successful. In contrast,

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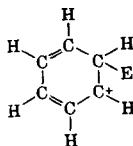
benzene and its homologs undergo substitution reactions much more readily than the alkanes. The following equations illustrate a few of the many substitution reactions so characteristic of benzene hydrocarbons:



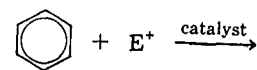
**MECHANISM OF AROMATIC SUBSTITUTIONS.** It is thought that the initial step in aromatic electrophilic substitutions is similar to the first step in additions to ethene double bonds, that is, pi-electron attack by the electrophilic group  $\text{E}^+$  (an ion such as  $\text{Cl}^+$ ,  $\text{Br}^+$ , or  $\text{NO}_2^+$ ), accompanied by the formation of a carbonium ion:<sup>1</sup>



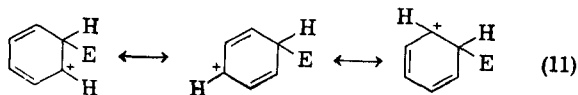
<sup>1</sup> The abbreviated formulas used in equation (11) are somewhat difficult to follow. Accordingly, the first one is shown in full detail as follows:



Note that four of the carbons retain the features of the benzene ring. Note also that the carbon which has only three valence bonds is electron-deficient and electrophilic.



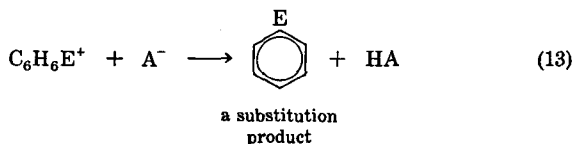
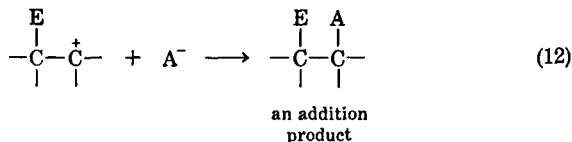
benzene electrophilic  
group



carbonium ion,  $\text{C}_6\text{H}_6\text{E}^+$

Because the plus charge of the carbonium ion originating from the alkene is localized on one carbon, Eq. (10), an anion adds to this carbon to complete the addition. The plus charge of the carbonium ion originating from benzene is thought to be distributed over the entire molecule rather than being localized on one carbon atom. The three resonance structures shown for  $\text{C}_6\text{H}_6\text{E}^+$  differ only in the placement of valence bonds and charges and not in placement of atomic nuclei. The actual structure of this carbonium ion is thought of as a hybrid of these resonance forms. Although the hybrid ion, with its delocalized charge, is of higher energy than a benzene molecule, it is of lower energy than a  $\text{C}_6\text{H}_6\text{E}^+$  ion, in which the charge is localized on one carbon, as for example, a particle represented by just one of the three contributing structures shown on the right of Eq. (11).

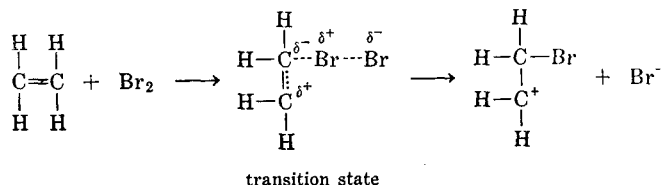
The two carbonium ions, the one from an alkene and the other from benzene, behave quite differently in the next steps, Eqs. (12) and (13). Both ions are high-energy, unstable particles and go through an energy-lowering step to form stable products. For the alkene carbonium ion with a localized plus charge, the preferred step is the addition of an anion, Eq. (12); for the benzene carbonium ion, the preferred step is the donation of a proton to an anion, Eq. (13), to regenerate the very stable aromatic resonance-hybrid  $\text{C}_6\text{H}_5\text{E}$ , which has a benzenelike structure:



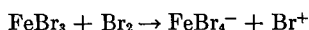
Now let us return to Eqs. (10) and (11) and note that, although no catalyst was indicated as being necessary for the formation of the

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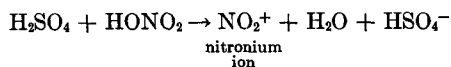
carbonium ion from the alkene, one was indicated for benzene. The single pair of pi electrons in an alkene is usually able to bring about polarization and ionization of certain molecules without the need of outside help:



In contrast, the six pi electrons in benzene, with their charges distributed over the entire molecule, are apparently unable to polarize the bromine molecule sufficiently to bring about addition. However, in the presence of  $\text{FeBr}_3$ ,  $\text{Br}^+$  does add to form  $\text{C}_6\text{H}_6\text{Br}^+$ . The  $\text{FeBr}_3$  is believed to aid the reaction by reacting with  $\text{Br}_2$  molecules to form the required  $\text{Br}^+$  ions:



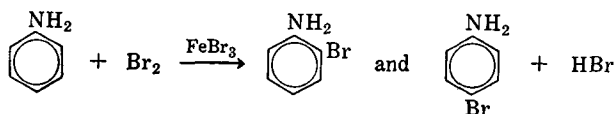
When benzene is nitrated, Eq. (7), sulfuric acid is employed as a catalyst. Like  $\text{FeBr}_3$ ,  $\text{H}_2\text{SO}_4$  reacts with a covalent molecule to produce a positive ion that can act as an electrophilic group in attacking the benzene ring:



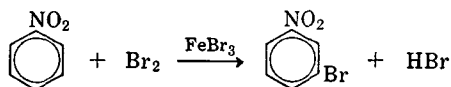
In concluding this discussion, let us again point out that we have dealt with electrophilic substitution only. Benzene hydrocarbons also undergo nucleophilic substitution, a phase of benzene chemistry that we shall not discuss.

**Directive Influences of Groups Attached to Benzene Ring.** The six hydrogens of the benzene ring are equivalent, so that the replacement of one hydrogen with another group does not lead to isomeric products. The replacement of a second hydrogen does lead to di-substituted isomers (*o*-, *m*-, and *p*-isomers), and it is a matter of considerable interest and importance as to which isomer or isomers will be formed in the largest amount.

To illustrate that there is a natural tendency for different amounts of *o*-, *m*-, and *p*-isomers to form, let us consider the replacement of a hydrogen with a bromine group in molecules of aniline and nitrobenzene. When aniline,  $\text{C}_6\text{H}_5\text{NH}_2$ , is brominated so as to replace only one hydrogen per molecule, the product consists mainly of *o*- and *p*-bromoaniline (very little *m*-bromoaniline is formed).



On the other hand, when nitrobenzene is brominated to form bromo-nitrobenzene, the product is mainly *m*-bromonitrobenzene:

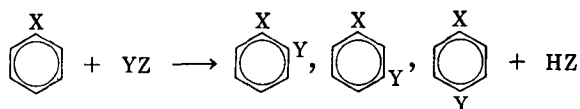


The foregoing examples show that certain groups, when attached to a carbon in a benzene ring, have the property of directing further substitution to the *ortho*- and *para*- positions, and others direct to the *meta*- position. The former are called *ortho*- and *para*-directing groups, the latter, *meta*-directing groups.

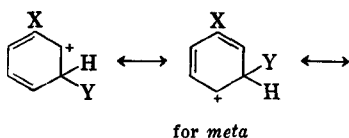
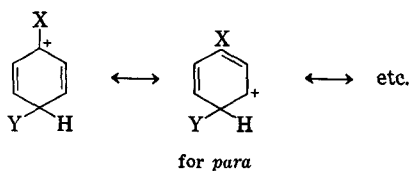
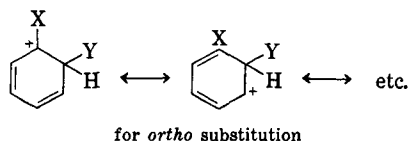
Examples of *o*- and *p*-directing groups:  $-\text{NH}_2$ ,  $-\text{OH}$ , alkyl radicals ( $-\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_3$ , etc.),  $-\text{F}$ ,  $-\text{Cl}$ ,  $-\text{Br}$ ,  $-\text{I}$ .

Examples of *m*-directing groups:  $-\text{NH}_3^+$ ,  $-\text{NO}_2$ ,  $-\text{COOH}$ .

The mechanism by which certain groups direct to *ortho* and *para* positions and others direct to the *meta* position is well understood. However, we shall not attempt a complete explanation but shall introduce a general idea to show the direction an explanation might take. First let us consider the following substitution reaction to form disubstitution products:



The first step is the formation of hybrid carbonium ion intermediates, such as (not all possible structures are shown):



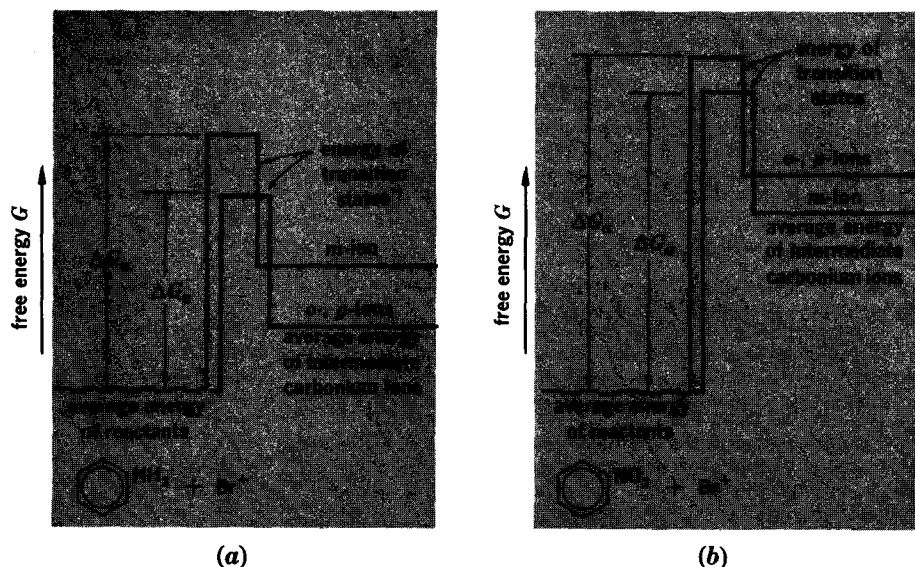
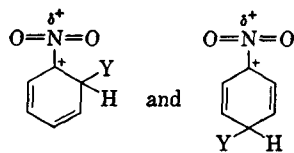


FIG. 26-3

(a) For aniline, the free energy of activation for the formation of the intermediate carbonium ion for *o*- and *p*-substitution is less than for the meta isomer. The product of the reaction will be mainly *o*- and *p*-bromoaniline. (b) The reverse is true for the bromination of nitrobenzene; consequently, *m*-bromonitrobenzene is the main product. Note that the activation energies in (b) are shown considerably higher than in (a).

Some of these structures are more stable than others, depending on the attraction for electrons by *X*. For example, the first structures shown for *ortho* and for *para* substitution would not be stable if *X* is the  $\text{—NO}_2$  group, owing to the strong attraction of oxygen for electrons, leaving the nitrogen relatively positive. This condition would tend to join a positive atom to a positive atom:



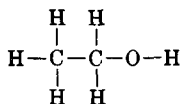
unstable *o*- and *p*-carbonium ions

Because the formation of the carbonium ion depends on the delocalization of the positive charge and because the nitro group decreases the number of contributing resonance structures for the delocalization in *o*- and *p*-carbonium ions, the hybrid ion for these will be less stable. This means that a higher activation energy will be required for the formation of the transition state leading to the *o*- and *p*-carbonium ions than to the *m*-carbonium ion. Hence the entering group takes mainly the *meta* position when *X* is a nitro group (see Fig. 26-3).

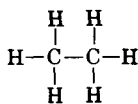
Conversely, when  $X$  tends to increase the number of stable contributing structures for the hybrid  $o$ - or  $p$ -carbonium ion or to decrease the number of stable contributing structures for the hybrid  $m$ -carbonium ion, *ortho* and *para* substitution will be favored.

## DERIVATIVES OF HYDROCARBONS

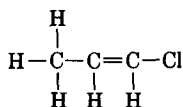
The hydrocarbons serve as the basis for the classification and systematic naming of all organic compounds. In this classification, a chain or ring type of nonhydrocarbon compound is considered to be derived from the hydrocarbon that contains the same carbon chain or ring. For example, ethyl alcohol is considered to be a derivative of ethane, and 1-chloropropene is considered to be a derivative of propene. It will be observed from the following formulas that these derivatives differ from the parent hydrocarbons in that hydrogen atoms have been replaced with other atoms or groups of atoms:



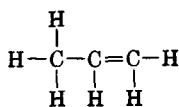
ethyl alcohol



ethane  
(parent hydrocarbon)



1-chloropropene



propene  
(parent hydrocarbon)

**Functional Groups.** Replacement of one or more hydrogen atoms of a hydrocarbon molecule with oxygen, chlorine, hydroxyl, nitrate, or other groups of atoms produces chemically active centers in an otherwise less active molecule. These groups are able to function in a variety of reactions and hence are referred to as **functional groups**. The compounds in which hydrogen atoms have been replaced in this way include alcohols, ethers, aldehydes, etc.

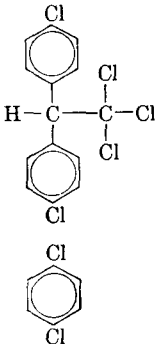
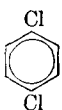
## HALOGEN DERIVATIVES

Although certain halogen derivatives are of value as such (see Table 26-1), many serve as intermediates in the synthesis of common organic substances from raw materials, such as coal, natural gas, and petroleum. The intermediate halogen compounds can be prepared from hydrocarbons by addition and substitution reactions discussed earlier in this chapter, or they may be prepared from nonhydrocarbon substances.

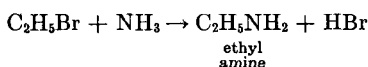
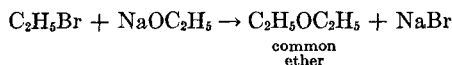
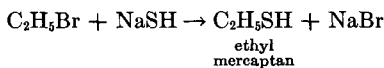
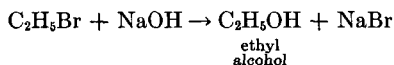


**PROPERTIES OF HYDROCARBONS;  
HALOGEN DERIVATIVES**

**TABLE 26-1**     *Halogen derivatives*

formula	common name	systematic name	uses
$\text{CCl}_4$	carbon tetra- chloride	tetrachloromethane	fire extinguisher, solvent
$\text{CHCl}_3$	chloroform	trichloromethane	solvent
$\text{CCl}_2\text{F}_2$	Freon-12	dichlorodifluoro- methane	compressor gas in refrigerators, propellant in aerosols and foams
$\text{CH}_2\text{BrCH}_2\text{Br}$	ethylene bromide	1, 2-dibromoethane	ethyl gasoline
	DDT	2, 2-Di-( <i>p</i> -chloro- phenyl)- 1,1,1-trichloroethane	insecticide
	<i>p</i> -dichloro- benzene	<i>p</i> -dichlorobenzene 1,4-dichlorobenzene	moth repellant

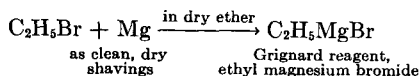
Several methods have been developed for replacing halogen atoms with other functional groups, leading to a great variety of organic compounds. We shall illustrate a few of these below, using ethyl bromide as the halogen derivative (ethyl iodide and ethyl chloride, but not ethyl fluoride, give the same reactions):



These reactions are quite general and are applicable to other alkyl bromides, chlorides, and iodides, for example,  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ , and to the halogen derivatives of other hydrocarbon series. However, when the halogen is attached to a carbon bonded to another carbon by a pi bond, as in  $\text{CH}_2=\text{CHCl}$  or  $\text{C}_6\text{H}_5\text{Cl}$ , the halogen is considerably more difficult to replace with other groups.

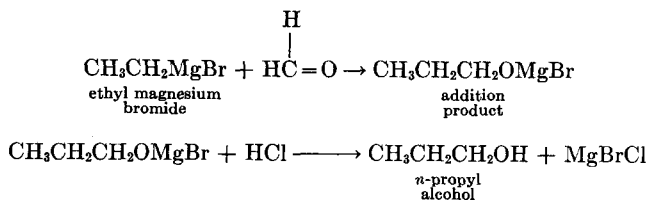
**GRIGNARD REAGENT.** In addition to replacement reactions of the type illustrated in the preceding section, halogen derivatives undergo several special kinds of reactions that are of considerable value in synthesizing organic compounds. We shall describe only one of these, the Grignard reaction, named after its discoverer, Victor Grignard. We shall again use ethyl bromide to illustrate the preparation of the reagent. However, chloride and iodide derivatives may be used, and the process may be applied to the halogen derivatives of other aliphatic hydrocarbons and to aromatic hydrocarbons, but not always with the same degree of success as that obtained with derivatives of alkane hydrocarbons.

Preparation of the reagent:

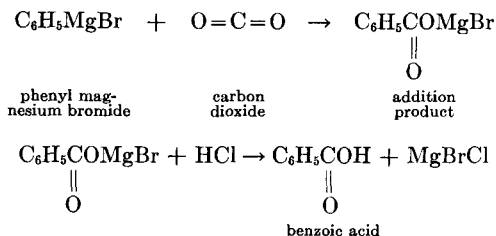


Utilization of the reagent:

A variety of substances react with the reagent to form an addition product that is then hydrolyzed with acids to form the final product. We shall describe two examples. In the first, the ethyl Grignard reagent and formaldehyde are used to produce *n*-propyl alcohol:



In the second example, the phenyl Grignard reagent and carbon dioxide are used to produce benzoic acid:

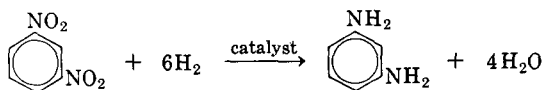


## DETERMINING STRUCTURES OF ORGANIC MOLECULES

During the first 100 years of the development of organic chemistry, the research chemist relied mainly on chemical reactions, elemental analyses (Chap. 9), and molecular weight determinations to give him clues to the structure of organic molecules. And he relied heavily on melting points and boiling points to differentiate between compounds

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very similar to one another, isomers, for example. Once the structure of one compound had been determined, that compound could be used to help establish the structures of other compounds. For example, if a certain dinitrobenzene had been established as the *meta* isomer, the diaminobenzene prepared from it by reduction was assumed to be the *meta* isomer also:



This brings up the question of how the structure of the first *meta* isomer was established, or for that matter, the structure of the first isomer in any series of derivatives. To explore this question briefly, let us go back to some of the early work on benzene and its homologs.

In every case where an exhaustive search has been made, three, and only three, isomers of di-substituted benzene have been isolated. For example, in dimethylbenzene,  $\text{C}_6\text{H}_4(\text{CH}_3)_2$ , three different compounds were shown to exist because of the difference in physical properties:

Isomer A: mp  $13^\circ$ ; bp  $138^\circ$

Isomer B: mp  $-25^\circ$ ; bp  $144^\circ$

Isomer C: mp  $-47^\circ$ ; bp  $139^\circ$

That the three compounds were isomers was shown by the experimental facts that all had the same percentage by weight of carbon and hydrogen and the same molecular weight.<sup>1</sup> The fact that only these three di-substitution isomers were shown to exist experimentally was one bit of evidence for the theory that benzene molecules are closed-chain (cyclic) molecules rather than open-chain molecules, because on this basis one predicts the existence of only three di-substitution isomers.

A method for solving the problem of which isomer is the *ortho* isomer, which the *meta*, and which the *para* was first devised by Wilhelm Koerner, a student of Kekulé. In 1878, he deduced that, if a third group is substituted for one of the remaining four hydrogen atoms in each member of a series of isomeric benzenes of the type  $\text{C}_6\text{H}_4\text{X}_2$ , the *ortho* compound should give two tri-substitution isomers, the *meta* three, and the *para* one.

To see why this is logical, let us imagine that we nitrate each of the isomeric xylenes in such a way that only one hydrogen per molecule is replaced with a nitro group. There are four hydrogen atoms on the

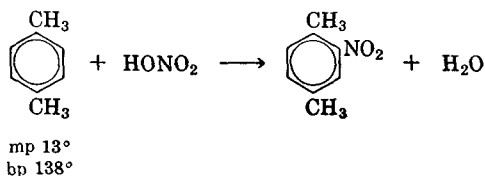
<sup>1</sup> Ethyl benzene,



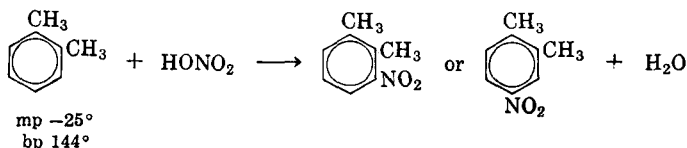
has the same composition and the same molecular weight as the three xylenes and is therefore isomeric with them. However, ethyl benzene is not a di-substitution product, as proved by its oxidation to benzoic acid (see page 688).

ring of a xylene molecule; the nitro group may replace any one of these four atoms. In some of the molecules the replacement occurs at one position, in other molecules it occurs at other positions; hence a mixture of compounds may be produced.

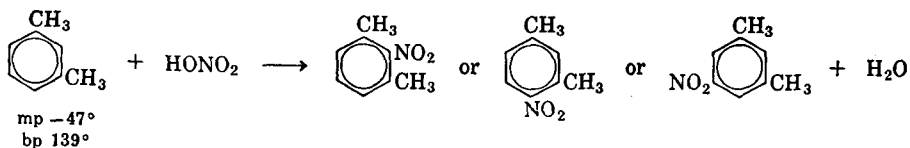
The nitration of *para*-xylene cannot result in a mixture, however, because replacement of any one of the four hydrogens will give rise to a compound in which the nitro group is at the same relative position, that is, adjacent to one methyl group but one place removed from the other methyl group:



*ortho*-Xylene can give rise to two products:



*meta*-Xylene can give rise to three:

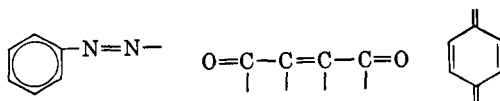


By nitrating each of the isomeric xylenes and then isolating the products, the chemist can identify the isomers. The one that melts at 13° yields only one tri-substitution product and hence is the *para*-xylene; the one that melts at -25° yields two products and hence is the *ortho*-xylene; the one that melts at -47° yields three products and hence is the *meta*-xylene.

Today, the organic chemist still uses to some extent the older methods to help him establish the structures of new compounds, but he has in addition modern tools which enable him to do the job more rapidly and with greater surety and which also allow him to confidently delve into the structures of very complicated molecules, such as are found in living cells. Two of the modern methods were discussed in Chap. 17, absorption spectra and nuclear magnetic resonance; a third, X-ray diffraction, was discussed in Chap. 7; and a fourth, tracer or tagged atoms, was discussed in Chap. 15.

## COLOR OF ORGANIC COMPOUNDS

Different substances have color because their molecules have the property of selectively absorbing wavelengths from white light (see Chap. 17). Saturated molecules of organic compounds do not selectively absorb in the visible portion of the spectrum; therefore, they are colorless. On the other hand, molecules with certain types of unsaturation (in which electrons have a particular freedom) remove specific wavelengths and transmit colored light. The particular types of electron vibrations present in colored compounds usually occur at places in the molecule where several atoms are joined alternately by double and single bonds. Here are three such groups of atoms, called **chromophores** (color bearers):



The exact color of a substance is determined not only by the type of chromophore present, but also by the nature of the molecule of which the chromophore is a part. Many different dyes can be made by introducing substituents, such as  $\text{—OH}$ ,  $\text{—NH}_2$ ,  $\text{—NHCH}_3$ ,  $\text{—SO}_2\text{OH}$ , into the molecules that contain a given color-forming group. The groups that contribute to or change the color of the dye are referred to as **auxochromes** (auxiliary color producers). The auxochromes generally have the additional function of making the dye fast to cloth or other articles by salt formation.

The synthetic dye industry was first developed in England in about 1860. By the turn of the century, Germany's vigorous research program carried out by industry and the universities had given that country almost complete control of the dye industry and, along with it, the organic chemical industry, including the manufacture of medicinal substances. After World War I, the United States gradually forged to the front and now leads the world in the production of organic chemicals. Our production of dyes, largely from intermediates obtained from coal tar, approaches 170 million lb annually.

## CHAPTER REVIEW

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### *Topics*

Controlled oxidation, addition reaction, unsaturated hydrocarbon, Markownikoff's rule, mechanism of a reaction, unsymmetrical alkene, carbonium ion, transition state, electrophilic reagent, nucleophilic reagent, substitution reaction, radical, saturated hydrocarbon, aromatic substitution, directive influences in benzene ring, *o*- and *p*-directing groups, *m*-directing groups, mechanism of directive influence, derivatives of hydro-

carbons, functional group, halogen derivatives, Grignard reaction, determination of structure, color of organic compounds, chromophore, auxochrome.

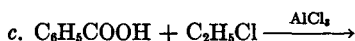
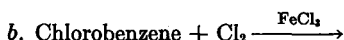
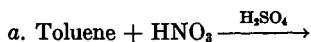
### Exercises

1. Is 2-ethyl heptane soluble or insoluble in water; melting point above or below 25°C; boiling point above or below 50°C; density less or more than 1 g/ml?
2. Predict which of each pair below will have the higher boiling point. Upon what did you base your prediction?
  - a. 1-Heptane and toluene
  - b. 1-Heptane and 1-hexane
  - c. 1-Heptane and 1-heptene
  - d. 1-Heptane and 2-methylhexane
3. Write equations to illustrate the reactions that occur when each of the following is completely burned in air: *o*-xylene, propyne, kerosene.
4. Show with equations the probable reaction occurring for each of the following:
  - a. Propene is oxidized in a water solution of  $\text{KMnO}_4$ .
  - b. 2-Butene is oxidized in a water solution with ozone.
  - c. Ethyl benzene is oxidized in acid solution with  $\text{KMnO}_4$ .
5. Which would liberate considerably more heat upon combustion, or would the heats of combustion be approximately the same:
  - a. A liter of methane or a liter of ethane, both measured at STP?
  - b. A liter of 1-octane or a liter of 1-nonane?
6. Calculate the heats of combustion at 25°C of ethane, ethene, and ethyne, using the data in Table 16-6.
7. Write the equation and name each product for the complete addition of:
  - a. Hydrogen to toluene
  - b. Hydrogen bromide to 2-methylbutene
  - c. Chlorine to 2-butyne
8. Is Markownikoff's rule of help in predicting which isomer will be formed by the addition of hydrogen chloride to 2-pentene? Write the structure of the carbonium ion that would lead to the formation of 2-chloropentane; to the formation of 3-chloropentane.
9. The reaction  $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$  takes place at a moderate rate at a certain temperature. Does this mean that every collision between a chlorine molecule and a methane molecule results in a reaction? Explain. Why will this reaction proceed at a faster rate at a higher temperature?
10. To what does the *transition state* refer with respect to the reaction shown in Exercise 9?
11. What is believed to be the mechanism of the reaction  $\text{C}_2\text{H}_6 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{HCl}$ ? Ultraviolet radiation may be employed in the success-

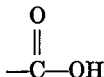
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ful execution of this reaction. What part does it play? One might find  $C_4H_5Cl$  among the reaction products. Account for its formation.

12. Iron(III) chloride is used to catalyze the reaction  $C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$ . How does it do this?
13. Which of the following indicated reactions give mainly *o*- and *p*- products? Which give mainly the *m*-isomer? In each case, write the equation for the reaction, showing only the isomers that probably form in the largest amounts:



14. What is meant by *delocalization of a positive charge* with respect to a carbonium ion involving a benzene ring? Would a



group attached to a carbon of the ring tend to reduce the delocalization of the positive charge of the carbonium ion, thus leading to *o*- and *p*-substitution? Explain.

15. Show with equations how the following compounds could be prepared from the indicated starting materials; any inorganic chemicals needed may be assumed to be available:
- a. 2-Butanol,  $CH_3CHOHCH_2CH_3$ , from 2-bromobutane
- b. Methyl-1-propanol from formaldehyde,  $HCHO$ , and 2-bromopropane
- c. Acetic acid,  $CH_3COOH$ , from bromomethane and carbon dioxide
16. Starting with 1,2,3-trichlorobenzene, replacement of another hydrogen with chlorine could give rise to how many isomeric tetrachlorobenzenes? Starting with 1,2,4-trichlorobenzene, how many isomeric tetrachlorobenzenes are possible?
17. Benzene is a colorless compound, and azobenzene,  $C_6H_5-N=N-C_6H_5$ , is orange colored. Does this mean that the former does not give an absorption spectrum and the latter does? Explain.
18. Why is a colored compound not necessarily a dye?
19. What are some vibrational movements (see Fig. 17-4) that  $C_3H_8$  would have but  $C_2H_6$  would not?

SUPPLEMENTARY READING

Allinger, N. L.: "Energy Relations in Teaching Organic Chemistry," *J. Chem. Educ.*, **40**: 201 (1963).

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Jones, G.: "The Markonikov Rule," *J. Chem. Educ.*, **38**: 297 (1961).  
Landgrebe, J. A.: "A Simple Kinetic Investigation of an Organic Reaction Mechanism," *J. Chem. Educ.*, **41**: 567 (1964).  
Mohacsi, Erno: "Characteristic NMR Spectral Positions for Hydrogen in Organic Structures," *J. Chem. Educ.*, **41**: 38 (1964).



# OXYGEN DERIVATIVES

## OF HYDROCARBONS



In this chapter we shall deal with simple derivatives that result from replacing one, two, or three hydrogen atoms in hydrocarbon molecules with oxygen atoms or hydroxyl groups. Although we shall tend to restrict the presentation to the first few members of the alkane series and to benzene, it should be borne in mind that the same derivatives are possible for the higher members of the two series, and in increasing numbers because of isomerism. Also, the many other series of hydrocarbons can give rise to the same derivatives, subject to some limitations due to the influence of multiple bonds, ring systems, or other unusual features of their molecules.

### ALCOHOLS

Derivatives whose molecules contain one or more hydroxyl ( $\text{—OH}$ ) groups in place of hydrogen atoms are known as **alcohols**. Hundreds of alcohols, derived from the alkanes, alkenes, alkynes, and other hydrocarbons, are known. The simplest alcohols are derived from the alkanes and contain only one hydroxyl group per molecule. These have the general formula  $\text{ROH}$ , where R is an alkyl radical of the composition  $\text{—C}_n\text{H}_{2n+1}$ . The first few members are as follows:

$\text{CH}_3\text{OH}$	methanol (methyl alcohol)
$\text{C}_2\text{H}_5\text{OH}$	ethanol (ethyl alcohol)
$\text{C}_3\text{H}_7\text{OH}$	the propanols
$\text{C}_4\text{H}_9\text{OH}$	the butanols

Ball-and-stick model of a molecule of ethyl alcohol,  $C_2H_5OH$ .

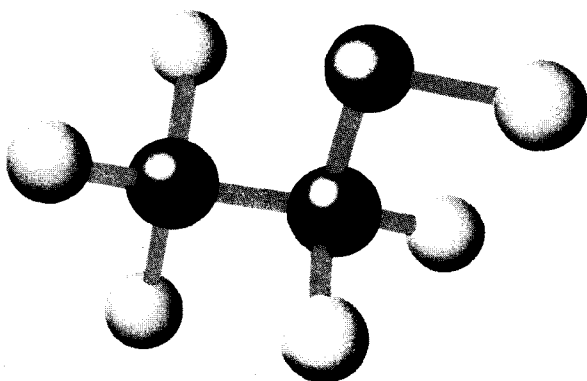
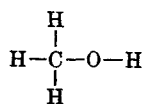
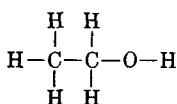


FIG. 27-1

Because all the hydrogen atoms in molecules of methane or in molecules of ethane are equivalent, there are no isomeric methanols or ethanols. The structural formulas for these two compounds are



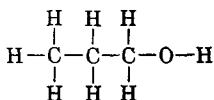
methanol  
(methyl alcohol)  
bp  $65^\circ$



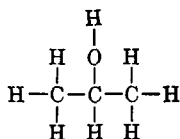
ethanol  
(ethyl alcohol)  
bp  $78.5^\circ$

A ball-and-stick model of a molecule of ethanol is shown in Fig. 27-1. In such models, the sticks joining carbon and hydrogen represent  $sp^3-s$  orbital bonds characteristic of alkane hydrocarbons; the bond joining the carbon and oxygen results from the overlap of an  $sp^3$  orbital of carbon and a  $p$  orbital of oxygen.

In the case of propane, the hydrogen atoms attached to the middle carbon are not equivalent to the hydrogen atoms attached to the end carbons. Replacement of a hydrogen atom on an end carbon with a hydroxyl group forms an alcohol that is different from the alcohol formed by replacement of a hydrogen on the middle carbon. Both of these alcohols are well known:



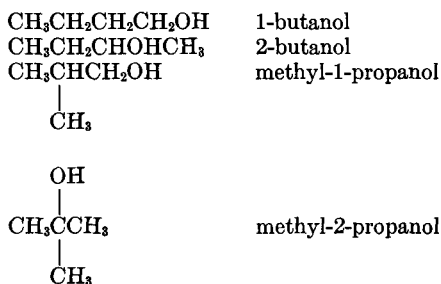
1-propanol  
(normal propyl alcohol)  
bp  $97^\circ$



2-propanol  
(isopropyl alcohol)  
bp  $82^\circ$

There are four butyl alcohols. Their semistructural formulas and systematic names are as follows.

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OF HYDROCARBONS**



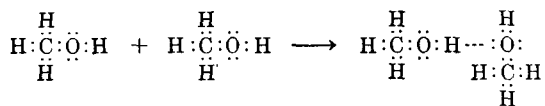
**Nomenclature.** The name of the hydrocarbon radical along with the word *alcohol* suffices for naming the first few members. Methyl alcohol, ethyl alcohol, and normal propyl alcohol are examples. Unfortunately, people are prone to consider the word *alcohol* as the only significant part of the name; many have lost their lives by drinking alcohol that was not ethyl alcohol. Consequently most manufacturers now use the systematic names instead of common ones, that is, methanol instead of methyl alcohol, ethanol instead of ethyl alcohol.

In the systematic naming of simple and complex alcohols alike, the following principles are followed:

1. The longest carbon chain that contains the hydroxyl group is considered the parent compound.
2. The *-e* in which the name of this carbon chain ends is changed to *-ol*.
3. The location of the hydroxyl and any other groups is shown by the smallest possible numbers.

These principles are illustrated in the preceding section in the case of methanol and ethanol and the isomeric alcohols with the formulas,  $\text{C}_3\text{H}_7\text{OH}$  and  $\text{C}_4\text{H}_9\text{OH}$ .

**Physical Properties.** In contrast to methane (boiling point  $-161^\circ$ ), methyl alcohol boils at  $65^\circ$ ; and in general, other alcohols boil at considerably higher temperatures than their parent hydrocarbons. This is thought to be due to the *association* of alcohol molecules through hydrogen bonding (the dashed line indicates the hydrogen bond):



It will be remembered that water has a relatively high boiling point for the same reason.

Also, unlike the parent hydrocarbons, the alcohols with low molecular weights are very soluble in water. This, too, is accounted for on the basis of hydrogen bonding between the hydroxyl group of the alcohol and the water molecules. However, as the molecular weight

increases, the van der Waals forces between the hydrocarbon portions of the alcohol molecules become more effective in attracting alcohol molecules to each other, thereby offsetting the effect of hydrogen bonding. For this reason, methyl alcohol is soluble in water in all proportions, whereas 1-decanol ( $C_{10}H_{21}OH$ ) is insoluble.

The location of the hydroxyl group on the carbon chain and the amount of branching have an important bearing on the melting and boiling points and on the solubility in water.

The properties of certain alcohols are summarized in Table 27-1.

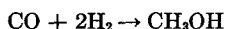
*Saturated aliphatic alcohols*

TABLE 27-1

alcohol	formula	melting point, °C	boiling point, °C	density	solubility in 100 g of water
methanol	$CH_3OH$	- 98	65	0.793	completely miscible
ethanol	$CH_3CH_2OH$	-117	78	0.789	completely miscible
1-propanol	$CH_3CH_2CH_2OH$	-127	97	0.804	completely miscible
1-butanol	$CH_3CH_2CH_2CH_2OH$	- 89	118	0.810	9 g at 15°
1-pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	- 78	138	0.817	2.7 g at 22°
1-hexanol	$CH_3CH_2CH_2CH_2CH_2CH_2OH$	- 52	156	0.820	slight

**Chemical Properties.** In contrast to the paraffin hydrocarbons, the alcohols are quite active chemically, because they enter into a number of reactions that involve the hydroxyl group. The hydroxyl group, therefore, is the functional group that characterizes alcohols. Only two of the characteristic properties will be mentioned here: (1) reactions that involve the elimination of a molecule of water to form ethers, esters, and unsaturated hydrocarbons and (2) partial oxidation to form aldehydes, ketones, and acids. Because of these properties, the alcohols are starting materials in the synthesis of many useful substances. Specific examples are given in the sections that follow.

**Common Alcohols.** **METHYL ALCOHOL.** Methyl alcohol (methanol, wood alcohol) was once made largely by the destructive distillation of hardwoods, such as birch, beech, oak, and maple. One cord of wood yielded about 225 gal of an aqueous distillate containing up to 6 per cent methyl alcohol and 10 per cent acetic acid. Today about 99 per cent of our output is produced by the catalytic hydrogenation of carbon monoxide:

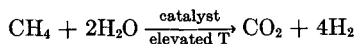
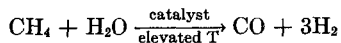


A catalyst ( $ZnO$ ,  $Cr_2O_3$ ) and elevated temperature and pressure are required for the success of the reaction.

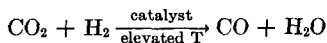
The carbon monoxide and hydrogen needed for the synthesis have long been made from coal by the water gas method (see Chap. 6). Recently, the low cost of methane from natural gas has led to the

## OXYGEN DERIVATIVES OF HYDROCARBONS

production of much of the carbon monoxide and hydrogen from this source. When methane and steam are passed over a catalyst the following reactions occur:

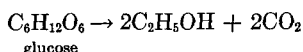
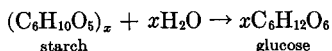


The carbon dioxide formed in the process is catalytically reduced:

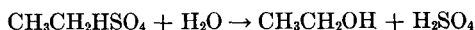


Our annual production of methyl alcohol is about 275 million gal. It is used chiefly in the manufacture of formaldehyde, and as a radiator antifreeze, a denaturant for ethyl alcohol, and a solvent for shellac and varnishes. Methyl alcohol may cause death when taken internally.

**ETHYL ALCOHOL.** Ethyl alcohol (ethanol, grain alcohol) is the physiologically active ingredient of beer, wine, and whiskey. It has been produced for centuries by the fermentation of *carbohydrates*. In the fermentation processes, organic compounds are broken down into simpler compounds by the action of **enzymes**. Enzymes are complex organic compounds that originate in living organisms. The production of ethyl alcohol from *starches* (corn, potatoes, rice, rye, etc.) involves first the enzymatic conversion of the starch into sugar (glucose). The sugar is then converted into alcohol and carbon dioxide by the action of *zymase*, an enzyme produced by living yeast cells. The fermentation must be carried out in dilute water solutions, because the yeast cells cannot live and multiply in concentrated sugar or alcohol solutions. The dilute alcohol solutions thus produced are distilled if a more concentrated product is desired. Alcohol produced from starches is used largely in beverages. The reactions are



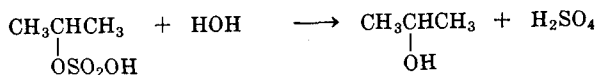
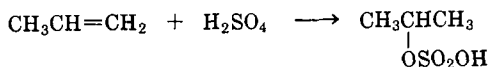
Industrial ethyl alcohol (annual production about 500 million gal) is mostly prepared by two methods: (1) fermentation of black-strap molasses from sugar cane and (2) the indirect addition of water to ethene, a by-product of the cracking of hydrocarbons to obtain gasoline. The equations for the latter reactions are



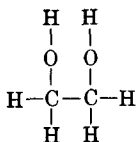
*Denatured alcohol* is ethyl alcohol that contains an ingredient that renders it unfit for drinking. Methyl alcohol is sometimes used for this purpose. Industrial ethyl alcohol sells at about 50 cents/gal.

**ISOPROPYL ALCOHOL.** Isopropyl alcohol, 2-propanol, does not pro-

duce intoxication, as does ethanol, and is not nearly so toxic as methanol, being only slightly more toxic than ethanol. It is used as a substitute for ethanol in certain drug preparations (rubbing alcohol, for example), in antifreeze mixtures, and as an intermediate in the synthesis of other chemicals, acetone being the most important. United States production, about 190 million gal annually (39 cents/gal in bulk quantities), is based on the indirect addition of water to propene (review Markownikoff's rule):



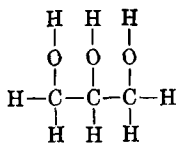
**DI- AND TRIHYDROXY ALCOHOLS.** The simplest and most important alcohol that contains two hydroxy groups is **ethylene glycol**. It is prepared commercially from ethene:



ethylene glycol, or  
1,2-dihydroxyethane

It is extensively used as a permanent antifreeze for automobile radiators.

The most important trihydroxy alcohol is **glycerol**, a derivative of propane:



glycerol, or  
1,2,3-trihydroxypropane

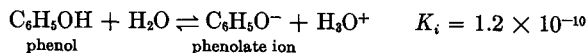
Glycerol is a by-product in the manufacture of soap and is also synthesized from propene.

## PHENOLS

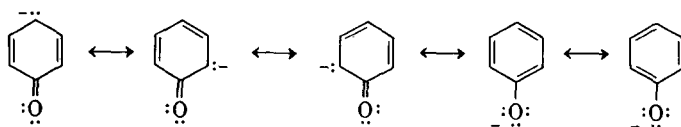
The properties of a functional group depend to some extent on the type of carbon ring or chain to which it is attached. The hydroxyl group provides excellent examples of this statement. When attached to the carbon of an aliphatic hydrocarbon, the hydrogen of the hy-

## OXYGEN DERIVATIVES OF HYDROCARBONS

dioxide ( $-\text{OH}$ ) radical does not ionize appreciably in water ( $K_i$  is about  $1 \times 10^{-16}$ ), and water solutions of alcohols therefore are neutral. When attached to a carbon of the benzene ring, the hydrogen of the hydroxide radical does ionize to a small extent. Hence water solutions of such aromatic derivatives contain an appreciable concentration of the hydronium ion and are weakly acidic:



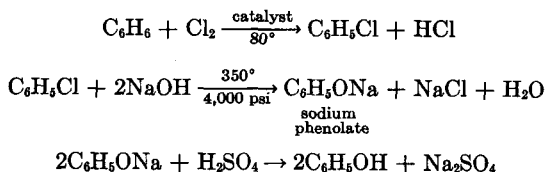
The tendency of phenol to act as an acid is attributed to the stabilization of the resulting phenolate ion by resonance energy. Several valence-bond structures can be written, so that a resonance hybrid structure is assumed to exist:



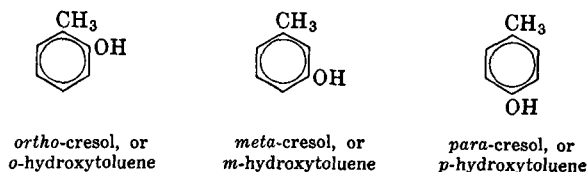
The hydroxy derivatives of aromatic hydrocarbons are called **phenols** rather than alcohols. The general formula for a phenol is  $\text{ArOH}$ , where Ar represents an aromatic hydrocarbon radical, for example,  $\text{C}_6\text{H}_5-$ ,  $\text{CH}_3\text{C}_6\text{H}_4-$ .

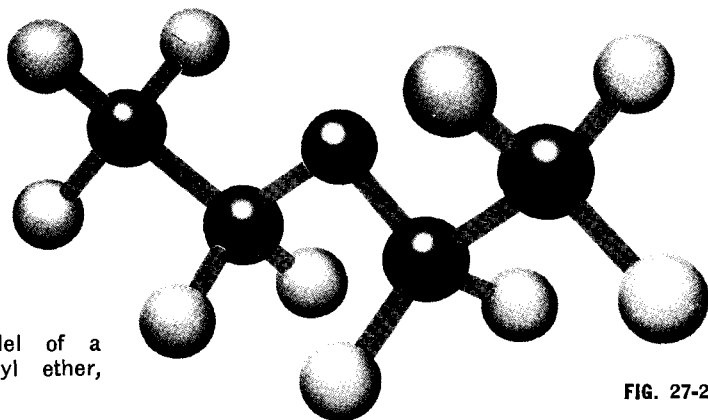
*Phenol*,  $\text{C}_6\text{H}_5\text{OH}$ , the first member of the phenols, is also known as *carbolic acid*. It is extremely destructive in its action on animal tissue; in dilute solutions, it is an excellent antiseptic.

Phenol is widely used in the synthesis of dyes, drugs, plastics, and other chemicals. For example, it is the starting point for the synthesis of salicylic acid, oil of wintergreen, and aspirin. The annual production of phenol in the United States is about 750 million lb. Of this, about 35 million lb is obtained directly from coal tar. The remainder is synthesized from benzene by a variety of methods. In one process, benzene is first converted to chlorobenzene, followed by replacement of chlorine with the hydroxide group:



The *cresols* are the hydroxy derivatives of toluene. Three isomers exist; their formulas are as follows:





Ball-and-stick model of a molecule of diethyl ether,  $C_2H_5OC_2H_5$ .

FIG. 27-2

*Creosote oil*, a coal-tar fraction, contains a large proportion of phenols; it is widely used as a wood preservative.

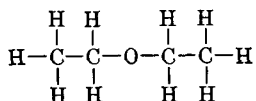
## ETHERS

The ethers are a class of compounds that contain two similar or dissimilar hydrocarbon radicals in combination with an atom of oxygen. Although hundreds of ethers are known, we shall center our attention on a few that are derived from the alkane hydrocarbons, that is, those in which the general formula is  $ROR'$ .  $R$  and  $R'$  are alkyl radicals and may or may not be the same. Examples are:

$CH_3OCH_3$	dimethyl ether
$CH_3CH_2OCH_2CH_3$	diethyl ether
$CH_3OCH_2CH_3$	methyl ethyl ether
$CH_3CH_2CH_2OCH_2CH_2CH_3$	di- <i>n</i> -propyl ether

Unlike alcohols, the ethers do not form associated molecules by means of hydrogen bonds. Hence the boiling point of an ether is considerably below the boiling point of the alcohol with the same number of carbon atoms. For example, ethyl alcohol is isomeric with dimethyl ether (both have the formula  $C_2H_6O$ ); yet dimethyl ether is a gas and ethyl alcohol is a liquid at room temperature. Furthermore, the ethers are either sparingly soluble or insoluble in water.

Common ether, the most widely used general anesthetic, is diethyl ether with the structural formula



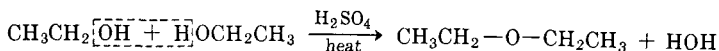
A model of a diethyl ether molecule is shown in Fig. 27-2.

Ethers are often prepared by the dehydration of the proper alcohol. Thus, diethyl ether is prepared by heating ethyl alcohol with concentrated sulfuric acid to a temperature of about  $140^\circ C$  and main-



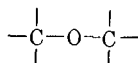
## **OXYGEN DERIVATIVES OF HYDROCARBONS**

taining that temperature till the reaction is complete. The reaction may be summarized by the following equation:



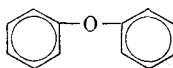
In addition to its use as an anesthetic, diethyl ether is widely employed as a solvent for fats, waxes, and other substances insoluble in water. It must be used with caution, however, because it is highly inflammable.

The functional group that is characteristic of ethers, the

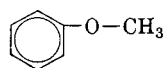


group, is not very active chemically; hence ethers as a class are not very active.

Ethers of the type  $\text{Ar—O—Ar}$  and  $\text{Ar—O—R}$  are also common. An example of each type follows:



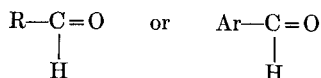
diphenyl ether



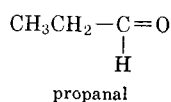
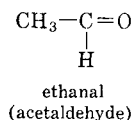
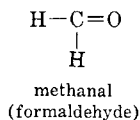
methyl phenyl ether

## **ALDEHYDES**

The aldehydes are a group of compounds with the general formula



In the first member of the aldehydes derived from the paraffin series, R is hydrogen; in the other members R is a usual alkyl radical. It is obvious from the general formula that aldehyde molecules differ from the parent hydrocarbon molecules in that two hydrogen atoms on an end carbon have been replaced with a single oxygen atom. The first few members derived from the methane series are

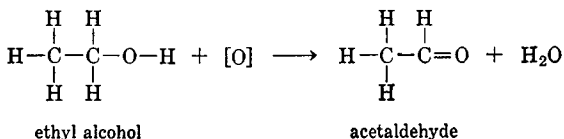


Systematic naming involves changing the end of the name of the parent hydrocarbon from *-e* to *-al*. The common names of the first two members, *formaldehyde* and *acetaldehyde*, are used by chemist and layman alike, instead of the systematic names.

Aldehydes are prepared by the mild oxidation of alcohols. Inasmuch as the aldehyde group is always located at the end of a carbon chain, the hydroxy group to be oxidized must also be located at the end of a

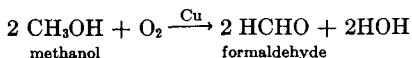
carbon chain. Alcohols of this type, that is,  $\text{—CH}_2\text{OH}$ , are called *primary alcohols*.

Oxidizing agents of the type  $\text{H}_2\text{O}_2$ ,  $\text{KMnO}_4$ , and  $\text{K}_2\text{Cr}_2\text{O}_7$  are used. The oxidation is usually carried out in solution so that the temperature cannot rise above the boiling point of the mixture. Further, the solution may be jacketed with an ice bath or other cooling medium to keep the temperature as low as necessary. Under these conditions, oxidation of the organic molecule will occur only at reactive points in the molecule. With the alcohols, only the portion of the molecule that is joined to the hydroxyl group is susceptible to oxidation. The following equation shows the overall oxidation, the brackets indicating that the oxygen is derived from unstable oxygen compounds:



Use of this method of controlled oxidation is limited to research work and to the manufacture of fine chemicals because of the high cost of the oxidizing agents.

For large-scale syntheses, oxidation is achieved with atmospheric oxygen whenever possible. At a moderate temperature and with the proper catalyst, oxygen often attacks the portion of the molecule most susceptible to chemical change without reacting with the remainder of the molecule. For example, formaldehyde is manufactured commercially by passing a mixture of air and methanol over a copper catalyst while maintaining the temperature in the reacting vessel at 550°:



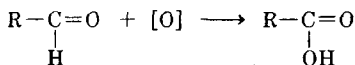
**Properties and Uses of Aldehydes.** Formaldehyde, a gas with a boiling point of  $-21^{\circ}\text{C}$ , is marketed as a 37 per cent water solution called *formalin* for use as an embalming agent, a preservative for biological specimens, and a fumigant. The important plastic known as Bakelite is produced by the reaction of formaldehyde with phenol. Production of formaldehyde in the United States is around 675 million lb annually.

Acetaldehyde is used chiefly as an intermediate in the production of other organic chemicals, especially acetic acid, 1-butanol, and ethyl acetate.

Benzaldehyde,  $\text{C}_6\text{H}_5\text{CHO}$ , an aldehyde derived from benzene by replacing a hydrogen with the aldehyde group, is used principally as an intermediate for the manufacture of dyes and drugs.

The aldehydes as a class are very reactive compounds. They are easily converted to the corresponding acid by controlled oxidation.

## OXYGEN DERIVATIVES OF HYDROCARBONS



Aldehydes also undergo a great variety of reactions involving the aldehyde group.

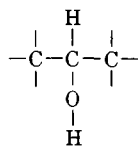
### KETONES

The ketones are a class of compounds with general formulas  $\text{RR}'\text{C}=\text{O}$ ,  $\text{ArAr}'\text{C}=\text{O}$ , and  $\text{RARC}=\text{O}$ . A few examples are

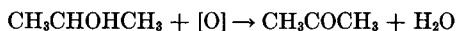


Notice that a ketone is very similar to an aldehyde, except that the  $=\text{O}$  is not bound to an end carbon.

Ketones are prepared by the partial oxidation of *secondary alcohols*, alcohols that have the structure



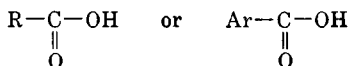
The oxidation of 2-propanol gives acetone:



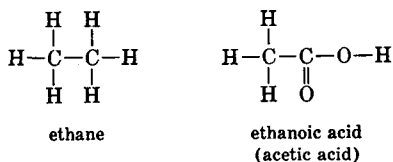
Acetone, the most important ketone commercially, is widely used as a solvent for waxes, plastics, and lacquers. More than 735 million lb is produced annually.

### CARBOXYLIC ACIDS

The simple carboxylic acids have the general formula



For those derived from the methane series, R represents H for the first member and  $C_nH_{2n+1}$  for the remaining members. Structurally, a carboxylic acid is considered to be derived by replacing the three hydrogen atoms on an end carbon with an atom of oxygen and a hydroxyl group:



The  $\begin{array}{c} \text{—C—O—H} \\ || \\ \text{O} \end{array}$  group is called the carboxyl group.

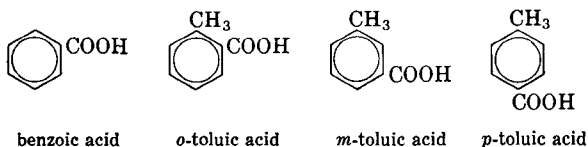
**Nomenclature.** Many of the carboxylic acids were isolated from natural sources long before systematic naming was introduced. They were given names indicative of their source, and these names have persisted. For example, the acid derived from methane was first obtained by the destructive distillation of ants and was called *formic acid* from the Latin *formica*, meaning ant. Similarly, the name *acetic acid* was derived from the Latin *acetum*, vinegar; *butyric* is from the Latin word meaning butter. Systematic naming involves replacing the final -e of the name of the hydrocarbon with -oic and using the word *acid*. Thus, the systematic names for formic and acetic acid are *methanoic acid* and *ethanoic acid*, respectively. Some of the important members that are derived from the methane series are listed in Table 27-2. They are frequently referred to as the fatty acids.

### Aliphatic carboxylic acids

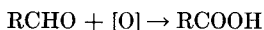
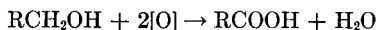
TABLE 27-2

formula	common name	occurrence	freezing point, °C	boiling point, °C
HCOOH	formic	ants, pine needles	8.4	100.7
CH <sub>3</sub> COOH	acetic	soured fruit juices, vinegar	16.6	118.2
CH <sub>3</sub> CH <sub>2</sub> COOH	propionic		-20.8	141.4
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	butyric	rancid butter, Limburger cheese	- 5.5	164.1
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOH	palmitic	fats (as esters)	62.8	
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COOH	stearic	fats (as esters)	69.6	

Carboxylic acids derived from aromatic hydrocarbons,  $ArCOOH$ , are quite common. Some examples are



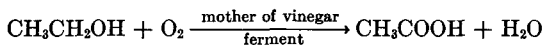
*Preparation of Carboxylic Acids.* There are numerous methods for preparing the RCOOH type of acid. The controlled oxidation of alcohols and aldehydes is widely used. In laboratory work, potassium dichromate and potassium permanganate are often used as the oxidizing agents. Atmospheric oxygen with a suitable catalyst is sometimes employed in commercial preparations:



Acetic acid is the most important carboxylic acid commercially. Production in the United States amounts to about 650 million lb annually, exclusive of that in vinegar. The acid is sold in the pure form as *glacial acetic acid*, so called because it freezes to an icelike solid on cold days. The melting point is 16.6°C. The acid is used in the manufacture of cellulose acetate, white lead for paint, dyes, and medicines.

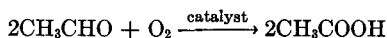
Acetic acid is usually prepared by the oxidation of ethyl alcohol or acetaldehyde, with atmospheric oxygen as the oxidizing agent.

ENZYME-CATALYZED OXIDATION OF ETHYL ALCOHOL. The alcohol in fermented fruit juices and fermented malt (cider, wines, beer) undergoes low-temperature oxidation to acetic acid in the presence of the proper enzyme and air:



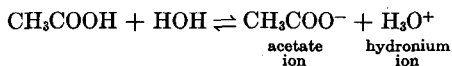
*Vinegar* produced in this manner is from 4 to 5 per cent acetic acid and is used almost exclusively as a condiment and food preservative. Its flavor is enhanced by the flavors in the cider, wine, or malt.

OXIDATION OF ACETALDEHYDE. In the presence of cobalt or manganese(II) acetate, acetaldehyde rapidly reacts with oxygen from the air, yielding acetic acid:



Most glacial acetic acid is now synthesized by this method.

*Properties of Carboxylic Acids.* The first four members derived from the methane series are completely miscible with water. As the molecular weight increases, however, the solubility in water decreases. Those which are soluble in water affect indicators, as do other acids and give a sour taste to the solution, but they are weak acids with low ionization constants:



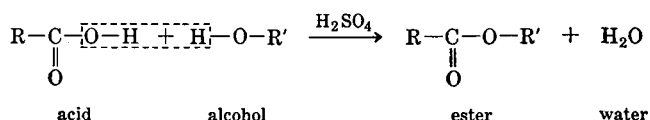
The lower members have an acrid odor; those from butanoic (C<sub>4</sub>) to heptanoic (C<sub>7</sub>) have disagreeable odors. The odors of rancid butter and strong cheese are due to acids in this group.

Benzoic and the toluic acids are comparable in strength to acetic acid. They are white solids and are only slightly soluble in cold water.

## ESTERS

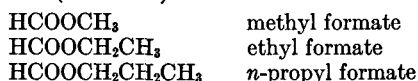
Esters are compounds that may be considered to be derived from acids by the replacement of the ionizable hydrogen with hydrocarbon radicals. General formulas for esters derived from carboxylic acids are  $\text{RCOOR}'$ ,  $\text{ArCOOAr}'$ ,  $\text{RCOOAr}$ , and  $\text{ArCOOR}$ .

There are many methods for the preparation of these compounds. In one method which is widely used and which indicates the structure of ester molecules, a molecule of water is lost when a molecule of an alcohol reacts with a molecule of a carboxylic acid. The overall reaction is as follows:

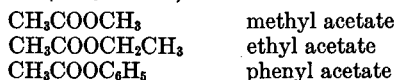


Each carboxylic acid gives rise to a homologous series of esters. Therefore the name of an individual ester is designed to show the acid and the hydrocarbon radical.

From *formic acid* ( $\text{HCOOH}$ ):



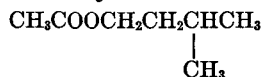
From *acetic acid* ( $\text{CH}_3\text{COOH}$ ):



From *benzoic acid* ( $\text{C}_6\text{H}_5\text{COOH}$ ):



The esters with low molecular weights are volatile liquids with pleasant fruity odors and are often found in fruits and flowers. The odor of banana is due to isoamyl acetate:



The flavor of pineapples is due to several esters (see Table 27-3).

### Composition of volatile oil in pineapple

TABLE 27-3

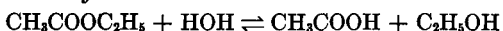
constituent	weight, mg/kg of fruit
ethyl acetate*	119.6
ethyl alcohol	60.5
acetaldehyde	1.35
ethyl acrylate*	0.77
ethyl <i>n</i> -caproate*	0.77
ethyl <i>i</i> -valerate*	0.39
total oil	190

\* Ester.

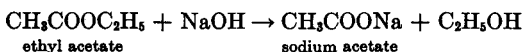
## OXYGEN DERIVATIVES OF HYDROCARBONS

Esters derived from acids and alcohols with high molecular weights are waxes. (These are not to be confused with the hydrocarbon type of wax, such as paraffin wax.) *Beeswax*, the material from which bees build the cells of the honeycomb, contains such esters as  $C_{25}H_{51}COOC_{26}H_{53}$  and  $C_{27}H_{55}COOC_{26}H_{53}$ . *Carnauba wax*, obtained from the leaves of a Brazilian palm and widely used as a component of automobile and floor waxes, is also composed of esters with high molecular weights.

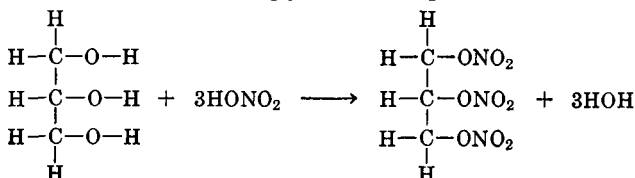
Hydrolysis converts an ester into the alcohol and the acid from which it is derived. Thus, the hydrolysis of ethyl acetate produces acetic acid and ethyl alcohol:



The hydrolysis goes to completion when the ester is boiled with dilute bases:



Up to this point the discussion of esters has involved only those derived from carboxylic acids. Several common and important esters are also derived from inorganic acids. A noteworthy example is glyceryl trinitrate (popularly called nitroglycerin), an ester obtained by the action of nitric acid on glycerol in the presence of sulfuric acid:



Nitroglycerin, an oily liquid, is a powerful explosive. When absorbed in wood flour or some other absorbent material it is called dynamite. Because it is fairly safe to handle in this form, it is the staple explosive for road building, mining, and many other peacetime operations.

The explosion of nitroglycerin involves the rapid oxidation of the carbon and hydrogen to carbon dioxide and water at the expense of the nitrate groups, which are reduced to nitrogen and to oxides of nitrogen. All the products are gases. As in all combustions, great heat is evolved. The hot gases formed exert terrific pressure in all directions, pushing aside obstacles in their path till their force of expansion is dissipated. Approximately 10,000 ml of hot gases is produced from 1 ml of liquid nitroglycerin.

## FATS

### OCCURRENCE

Many plant and animal materials—for example, peanuts, coconuts, cottonseed, olives, soybeans, cream, butter, cheese, and certain meats—contain large percentages of compounds called *fats*. The cereals as a rule are comparatively low in these compounds.

The fats are obtained from natural sources by a variety of methods. Heating and filtering the fatty tissues from hogs produces lard; churning milk separates the butter; and pressing and filtering seeds produces such oils as cottonseed oil and soybean oil. In some cases the fat is extracted from the natural source by solvents, such as carbon disulfide, ether, or alkanes with low molecular weight. (Fats are not soluble in water.)

The term *oil* generally refers to fats that are liquid at room temperature. This use of the word oil must not be confused with its use in such terms as kerosene oil, lubricating oils, and oil of wintergreen. The latter are not fats.

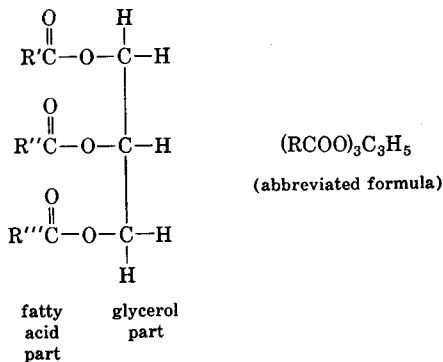
## HYDROLYSIS OF FATS; STRUCTURE

When lard, tallow, and other fats are boiled in dilute sodium hydroxide or subjected to the action of specific enzymes (in digestion), the fat molecules are completely hydrolyzed to form simpler molecules. *Glycerol*,  $\text{CH}_2\text{OHCHOHCH}_2\text{OH}$ , always constitutes a portion of the product, and acids with high molecular weights make up the remainder. The acids thus produced are fatty acids; the more common ones are

$\text{C}_{11}\text{H}_{23}\text{COOH}$	lauric acid	$\text{C}_{17}\text{H}_{33}\text{COOH}$	oleic acid
$\text{C}_{13}\text{H}_{27}\text{COOH}$	myristic acid	$\text{C}_{17}\text{H}_{31}\text{COOH}$	linoleic acid
$\text{C}_{15}\text{H}_{31}\text{COOH}$	palmitic acid	$\text{C}_{17}\text{H}_{29}\text{COOH}$	linolenic acid
$\text{C}_{17}\text{H}_{35}\text{COOH}$	stearic acid		

Lauric, myristic, palmitic, and stearic are unbranched *saturated* acids and are homologs of formic and acetic acids, that is, derivatives of the methane series. Oleic acid,  $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ , containing one double bond; linoleic, containing two; and linolenic, containing three, are *unsaturated* acids. Table 27-4 shows the relative amounts of fatty acids obtained by the hydrolysis of different fats.

In the fat itself, the glycerol portion and the fatty acid are joined by means of ester linkages. A *fat* may be defined as an ester of glycerol and long-chain carboxylic acids. A general structural formula is





## OXYGEN DERIVATIVES OF HYDROCARBONS

### *Fatty acids obtained from hydrolysis of fats and oils*

**TABLE 27-4** (in percentages\*)

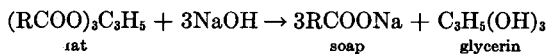
fat or oil hydrolyzed	saturated			unsaturated		
	lauric	palmitic	stearic	oleic	linoleic	linolenic
animal fats:						
butter	2-3	23-26	10-13	30-40	4-5	
lard		28-30	12-18	41-48	6-7	
tallow		24-32	14-32	35-48	2-4	
vegetable fats (oils):						
coconut	45-51	4-10	1-5	2-10	0-2	
olive		5-15	1-4	69-84	4-12	
peanut		6-9	2-6	50-70	13-26	
corn		7-11	3-4	43-49	34-42	
cottonseed		19-24	1-2	23-33	40-48	
soybean		6-10	2-4	21-29	50-59	4-8
linseed		4-7	2-5	9-38	3-43	25-58
tung		1-3	1-3	4-16	0-1	74-91†

\* The percentages do not total 100 because all the acids are not listed.

† An isomer of linolenic.

R', R'', and R''' may or may not be the same in the same molecule; they correspond to C<sub>11</sub>H<sub>23</sub>, C<sub>13</sub>H<sub>27</sub>, C<sub>15</sub>H<sub>31</sub>, C<sub>17</sub>H<sub>35</sub>, C<sub>17</sub>H<sub>33</sub>, C<sub>17</sub>H<sub>31</sub>, etc. It is interesting to note that in natural fats R is made up of an odd number of carbon atoms, and therefore the fatty acids derived from these fats have an even number of carbon atoms.

**SOAP.** In soap making, fat is heated in huge iron kettles with aqueous sodium hydroxide till the fat is completely hydrolyzed. The equation for the hydrolysis is

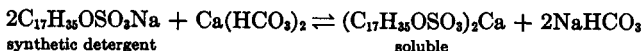
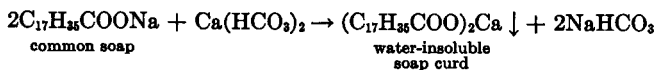


It is obvious from this equation that common soap may be a mixture of such compounds as sodium stearate,  $C_{17}H_{35}COONa$ , sodium palmitate,  $C_{15}H_{31}COONa$ , sodium oleate,  $C_{17}H_{33}COONa$ , and the sodium salts of other fatty acids. The soap is precipitated by the addition of salt. It is then removed by filtration, washed, and mixed with dyes, perfumes, or any other special ingredient. It is then permitted to harden, after which it is cut and pressed into cakes. Scouring powders contain a high percentage of an abrasive, such as volcanic ash or fine sand.

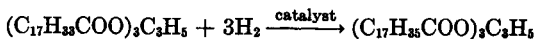
Soap functions in a variety of ways as a cleansing agent. It lowers the surface tension of water, thus enabling the water to moisten the material being washed more effectively; it acts as an emulsifying agent to bring about the dispersion of oil and grease (Fig. 11-5); and it adsorbs dirt.

The so-called *synthetic detergents* are of many types. In all of them a water-soluble saltlike group is attached to a hydrocarbon chain. A

typical example is  $C_{17}H_{35}-OSO_3Na$ . An important difference between ordinary soap and the synthetic detergents is that the latter do not form greasy precipitates with the polyvalent cations (for example,  $Ca^{2+}$  and  $Mg^{2+}$ ) that are normally present in unsoftened water.



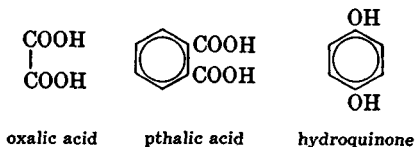
**Hydrogenation of Liquid Fats.** Study of Table 27-4 shows that, when hydrolyzed, liquid fats from vegetable sources yield a high percentage of unsaturated acids, whereas the solid fats from animal sources yield considerable amounts of saturated acids. This means that the R parts of the molecules of vegetable oils are more unsaturated than is true of the molecules of animal fats. A huge industry is based on the chemical conversion of liquid oils to solid fats by addition of hydrogen to some of the double bonds in the molecules of the oils. Hydrogenation is carried out at elevated temperatures in the presence of powdered nickel or some other catalyst. The following equation shows the complete hydrogenation of glyceryl trioleate to glyceryl tristearate:



*Margarine* is commonly made in the United States by blending hydrogenated fats (80 per cent) with skim milk, salt, lactic acid, and flavor producing bacteria. Most margarine is fortified with carotene (provitamin A).

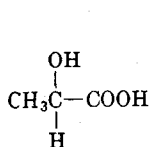
## MULTIPLE FUNCTION DERIVATIVES

Glycerol and fats are examples of compounds containing more than one functional group per molecule. Such molecules are very common among organic compounds. The functional groups may be of the same kind, as shown in the following examples:

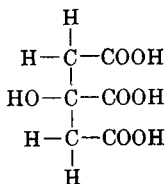


Or the functional groups may be of different kinds, so that the compound is both an alcohol and an acid (lactic acid, citric acid); or a ketone and an acid (acetoacetic acid); a phenol and an acid (salicylic acid); an ester and acid (aspirin, wintergreen); an aldehyde, ether, and phenol (vanillin); etc. The formulas for these examples are

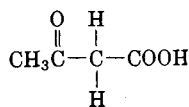
## DERIVATIVES CARBOXYLIC ACIDS



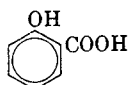
lactic acid



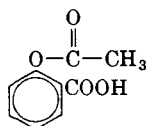
citric acid



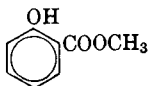
acetoacetic acid



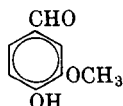
salicylic acid



aspirin or  
acetylsalicylic acid



wintergreen or  
methyl salicylate



vanillin  
(active component  
of vanilla)

## SULFUR ANALOGS

Since sulfur and oxygen are in the same periodic family, one might expect a companion series of alcohols, ethers, acids, etc., in which oxygen has been replaced by sulfur. In almost all cases the corresponding sulfur analogs do exist. Many examples of mercaptans or thioalcohols ( $\text{RSH}$ ), dithioacids ( $\text{RCSSH}$ ), thioketones ( $\text{R}_2\text{C}=\text{S}$ ), sulfides or thioethers ( $\text{R}-\text{S}-\text{R}$ ), and thioesters ( $\text{RCSSR}$ ), representing the sulfur analogs of alcohols, carboxylic acids, ketones, ethers, and esters, respectively, are known.

## SYNTHESIS PROBLEMS

The research organic chemist often desires to prepare a compound whose properties he would like to study, or he might simply be interested in seeing if he can devise methods for its preparation. In some cases, he might visualize the synthesis of an unknown compound, one not yet described in the chemical literature. He would base his scheme for a synthesis as far as possible on the kind of compounds available for the starting material and on known methods for changing one kind of functional group into another. He might work out on paper several schemes for the synthesis before beginning actual laboratory work.

Such paper exercises are also of value to the student of organic

chemistry in organizing and relating what may appear to be a large amount of somewhat unrelated material. Let us illustrate with two examples. Our examples will not involve unknown compounds, and the methods will involve only those which have already been presented in this and preceding chapters on organic chemistry.

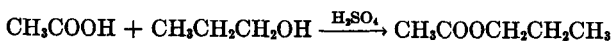
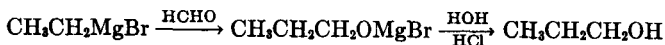
**PROBLEM 1** Devise a synthesis of *n*-propyl acetate from ethene:



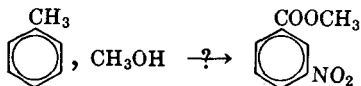
*Solution* (It may be assumed in this and other exercises that all inorganic substances needed, as well as carbon, carbon monoxide, and carbon dioxide, are available for the synthesis. No organic compound, except those given in the exercise, may be used unless its synthesis from the given organic compound(s) is shown.) We can analyze the synthesis by working backward a bit, that is, by noting that *n*-propyl acetate can be made from acetic acid and *n*-propyl alcohol. Hence our problem becomes



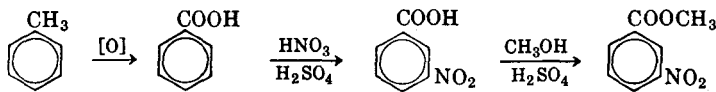
Acetic acid can be made by the oxidation of ethanol, which in turn can be made by the hydration of ethene. *n*-Propyl alcohol can be made from ethene by the Grignard reaction (see Chap. 26). We can show all this with outline equations (only the significant parts are shown, and the equations are not balanced) as follows:



**PROBLEM 2** Outline a synthesis of methyl *m*-nitrobenzoate from toluene and methanol:



*Solution*



## CHAPTER REVIEW

### Terms

Alcohol, association of molecules, functional group, di- and trihydroxy alcohols, phenol, cresol, ether, aldehyde, primary alcohol, ketone, secondary alcohol, carboxylic acid, carboxyl group, catalyzed oxidation, ester, fat,

saturated acid, unsaturated acid, soap, synthetic detergent, hydrolysis of fats, hydrogenation of fats, multiple function derivatives, sulfur analogs, synthesis problems.

### Exercises

1. Write structural formulas for all isomeric alcohols that have the molecular formula  $C_6H_{13}OH$ . Name each.
2. Ethanol is soluble in water in all proportions, but 1-hexanol is only slightly soluble in water. How may we account for this difference?
3. The synthesis of methanol is carried out at rather high pressure. Why?
4. Calculate the profit (?) that a moonshiner can make on a 100-lb bag of table sugar if he pays 10 cents/lb for the sugar and converts it into 80-proof whiskey that he sells for \$8/gal. Assume that he can recover no more than 60 per cent of the theoretical yield of alcohol. Eighty-proof whiskey is 40 per cent alcohol by volume. See Table 27-1 for density.
5. Write equations for the following:
  - a. Complete combustion of 2-propanol in air
  - b. Reaction of sodium with ethanol
  - c. Reaction of phenol and potassium hydroxide
6. Suggest a method for synthesizing 2-butanol.
7. Write structural formulas for all the isomeric ethers that have the molecular formula  $C_6H_{14}O$ . How many of these can you name?
8. Ethanol and dimethyl ether are isomers, having the molecular formula  $C_2H_6O$ . Based on structure, which one would be expected to have the higher vapor pressure; the higher boiling point; the greater solubility in water? Explain why in each case.
9. Consider again Exercise 1. How many of the isomers are classed as primary alcohols; as secondary alcohols?
10. List the compounds that can be obtained by subjecting 1-propanol to oxidation, using different oxidizing agents and reaction conditions.
11. Aldehydes are easily oxidized to carboxylic acids; ketones require more rigorous conditions, and the oxidation produces carboxylic acids with fewer carbon atoms per molecule than in the original ketone. Suggest a reason for these differences.
12. Name the following compounds:
  - a.  $CH_3CH_2CH_2OCH_3$
  - b.  $CH_3CH_2CH_2COOCH_3$
  - c.  $CH_3COCH(CH_3)_2$
  - d.  $CH_3CHOHCH_2CH_2CH_3$
13. What is the conjugate base of propanoic acid?  $K_a$  for propanoic acid is  $1.4 \times 10^{-5}$ . Would the pH of a water solution of sodium propanoate be 7, less than 7, or more than 7? Why?

14. Compare in a general way the  $pH$  of a 0.1  $M$  propanoic acid solution with that of a 0.1  $M$  propanoic acid solution that is also 0.1  $M$  with sodium propanoate. Account for these differences.
15. Calculate the  $pH$  of each of the solutions mentioned in Exercise 14.
16. Identify each of the following general formulas:  $RCOOR'$ ,  $ROH$ ,  $RCHO$ ,  $ROR'$ ,  $RR'CO$ ,  $RCOOH$ .
17. Write equations for:
  - a. Hydrolysis of *i*-propyl formate
  - b. Reaction of acetic acid and 2-butanol in the presence of  $H_2SO_4$
  - c. Reaction of *m*-toluic acid and ethanol in the presence of  $H_2SO_4$
18. Coconut oil is heated with aqueous sodium hydroxide till hydrolysis is complete. Name six compounds that are probably present in the reaction product.
19. Explain the cleansing action of a natural soap. How does the cleansing action of a synthetic detergent differ from that of a natural soap?
20. Rats and mice often eat natural soap. Do you think that natural soap would serve as a food for man? Explain.
21. Show with equations the reactions that occur when olive oil is hydrogenated.
22. What is meant by the sulfur analog of an alcohol; of a carboxylic acid?
23. Indicate with equations how the following syntheses could be carried out; the reagents available, in addition to those indicated in the problem, are  $CO$ ,  $CO_2$ , and any inorganic chemical:
  - a. Glucose  $\rightarrow$  ethyl acetate
  - b. Propene  $\rightarrow$  dimethyl ketone
  - c. Propene  $\rightarrow$  methyl-1-propanol
  - d.  $CO$ ,  $CO_2 \rightarrow$  acetic acid
  - e. Benzene  $\rightarrow$  methyl benzoate
  - f. Methanol  $\rightarrow$  diethyl ether
  - g. Ethene  $\rightarrow$  ethanol
  - h. Apple juice  $\rightarrow$  vinegar
24. Suppose that in carrying out your synthesis for (b) in Exercise 23, you started with 400 ml of propene, measured at  $0^\circ C$  and 5 atm, and obtained 2.0 g of pure dimethyl ketone. What is your percentage yield?
25. Phenol is soluble in 5 per cent  $NaOH$  solution; 1-hexanol is not. Account for these differences.
26. A druggist, in typing a label, made a typographical error, writing *carbonic* instead of *carbolic* acid. Is this a serious mistake?
27. The NMR spectrum of pure acetic acid,  $CH_3COOH$ , has three peaks. If acetic acid is mixed with large amounts of heavy water,  $D_2O$ , then repurified and tested, its NMR spectrum shows only two peaks in the same region. Why?

- Gillis, J. (trans. R. E. Oesper): "Kekule's Life at Ghent (1858-1867)," *J. Chem. Educ.*, **38**: 118 (1961).
- Hirsch, P. R.: "Effect of Liquid  $\text{NH}_3$  on Wood," *J. Chem. Educ.*, **41**: 605 (1964).
- Snell, F. D., and C. Snell: "Syndets and Surfactants," *J. Chem. Educ.*, **35**: 271 (1958).

## COMPLEX DERIVATIVES

## OF HYDROCARBONS



Most organic substances in plants and animals are composed of very complex molecules that, for the purpose of study and classification, are considered to be derived from hydrocarbons. However, the chemical processes by which plants and animals build complex molecules from simple ones do not involve prior formation of any "parent" hydrocarbons. In this chapter, we shall consider certain complex substances that are of natural origin—carbohydrates and proteins, for example—as well as some that are of synthetic origin.

## CARBOHYDRATES

## DEFINITION AND CLASSIFICATION

Carbohydrates are the simple sugars and the substances that, on hydrolysis, yield simple sugars. Originally, the name *carbohydrate* was used because the composition of most sugars, starch, and cellulose corresponds to that of hypothetical hydrates of carbon,  $C_x \cdot (H_2O)_y$ . The values of  $x$  and  $y$  may range from 3 to many thousands.

A comprehensive classification of the very large number of carbohydrates involves about a half-dozen main classes, with perhaps forty subclasses. A highly abridged classification is:

- |                                       |                                 |
|---------------------------------------|---------------------------------|
| 1. Monosaccharides                    | 3. Polysaccharides              |
| a. Pentoses, $C_5H_{10}O_5$           | a. Pentosans, $(C_5H_8O_4)_x$   |
| b. Hexoses, $C_6H_{12}O_6$            | b. Hexosans, $(C_6H_{10}O_5)_x$ |
| 2. Disaccharides                      |                                 |
| a. Hexose units, $C_{12}H_{22}O_{11}$ |                                 |



## MONOSACCHARIDES

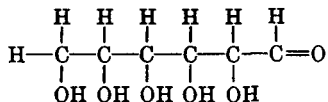
The monosaccharides are sugars that cannot be broken into simpler sugars by hydrolysis. Those which occur naturally have 3, 4, 5, 6, and 7 carbon atoms per molecule and are classified respectively as trioses, tetroses, pentoses, hexoses, and heptoses. Of this group, the *hexoses*,  $C_6H_{12}O_6$ , are most important. These are crystalline, water-soluble sugars of varying sweetness.

**Glucose.** Glucose,  $C_6H_{12}O_6$ , one of the isomeric hexoses, is a very important sugar in nature, both because of its widespread occurrence and because of its prominence in biological processes. It is the sugar into which all other carbohydrates are converted prior to oxidation in the body. (Other monosaccharides, such as fructose and galactose, are converted mainly into glucose in the liver before they enter the blood stream.) Glucose occurs as such in all ripe fruits, being especially abundant in grapes. Many other carbohydrates—for example, maltose, sucrose, starch, and cellulose—yield it on hydrolysis. Other names for it are grape sugar, blood sugar, and dextrose.

Some of the facts that have been considered in deducing the structure of glucose molecules are:

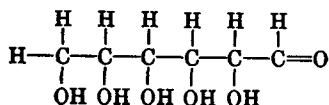
1. Replacement with hydrogen of all the oxygen groups in glucose by the action of hydrogen iodide and phosphorus yields *n*-hexane. The presence of this end product shows that in a glucose molecule there is an unbranched carbon chain that contains six carbon atoms.
2. Mild oxidation with silver nitrate forms an acid without loss of carbon. This shows the presence of an aldehyde group.
3. Treatment with acetic acid forms a pentaacetate; this indicates that the molecule contains five alcohol groups (OH).

The following structural formula is based on the foregoing considerations:



## OPTICAL ISOMERISM

We have just presented chemical evidence that glucose molecules contain six carbon atoms joined in an unbranched chain and that there are five alcohol groups and an aldehyde group as a part of the molecule. A surprising and interesting fact is that there are 15 other sugars whose molecules show the same composition. Put another way, there are 15 other sugars which have the same composition by weight, the same molecular weight, and which take part in the same chemical reactions. These 16 sugars all have the following structural formula.



An understanding of how the structural units in this formula can be arranged in 16 different ways became possible through the study of *optical isomerism* and the explanation of this type of isomerism in terms of *asymmetric carbon atoms*.

**Asymmetric Carbon Atoms.** A carbon atom to which are attached four different atoms or radicals is called an **asymmetric carbon atom**. When a molecule contains such an atom, the different groups can be positioned in space so as to form two kinds of molecules whose relationship to each other is that of an object and its mirror image. Hence the two forms are sometimes referred to as "right-handed and left-handed molecules." In a mirror your right hand looks like a left hand. Just as your right hand cannot be superimposed on your left hand so that every part will coincide, the molecule containing an asymmetric carbon cannot be superimposed on its mirror-image molecule so that every point will coincide.

To illustrate, consider *lactic acid*, the acid which is formed by the fermentation of sugar in milk and which has the formula  $\text{CH}_3\text{CHOH}-\text{COOH}$ . Because four different groups are attached to the middle carbon, namely  $-\text{CH}_3$ ,  $-\text{H}$ ,  $-\text{OH}$ , and  $-\text{COOH}$ , this is an asymmetric carbon atom.

Models showing the two possible arrangements in space of four groups around an asymmetric carbon atom. Note that the two forms have an object-mirror image relationship and that one cannot be superimposed on the other so that all points coincide.

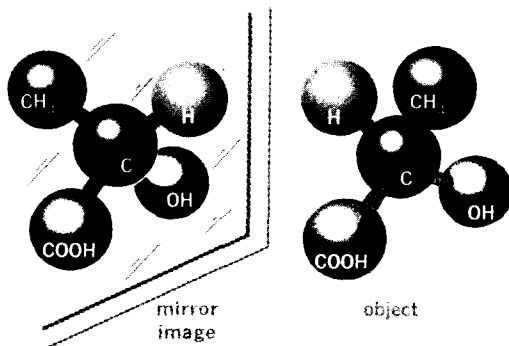


FIG. 28-1

Inasmuch as the valences of a carbon atom are directed toward the corners of an imaginary tetrahedron, the four groups can be located in space by positioning them at the corners of the tetrahedron, with the asymmetric carbon at the center (Fig. 28-1). Thus we find that two arrangements are possible, one the mirror image of the other. However, the two forms are not identical, because they are not superimposable. Isomers such as these, whose molecules differ only

## COMPLEX DERIVATIVES OF HYDROCARBONS

in the positioning of groups around asymmetric carbon atoms, are called optical isomers.

Because writing three-dimensional formulas of the type shown in Fig. 28-1 is time-consuming, the organic chemist generally uses two-dimensional formulas to indicate spatial position (Fig. 28-2). Such formulas are called *spatial* or *configurational formulas*.

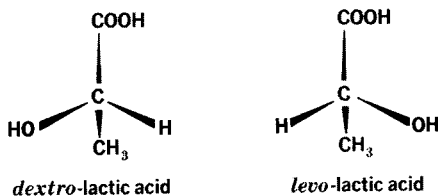


FIG. 28-2

Configurational formulas for the optical isomers of lactic acid. Wedges indicate that valence bonds extend from the asymmetric carbon atoms, shown in the plane of the paper, to groups lying behind the plane. Other wedges indicate valence bonds extending to groups lying above the plane of the paper. The point of a wedge is directed away from the viewer.

An important aspect of these optical isomers is that they rotate polarized light. Polarized light differs from ordinary light in that it vibrates in only one plane, whereas ordinary light vibrates in all directions perpendicular to the path of travel. Ordinary light becomes polarized when it passes through a crystal of calcite,  $\text{CaCO}_3$ , or a sheet of Polaroid. The beam that emerges is said to be plane-polarized (Fig. 28-3).

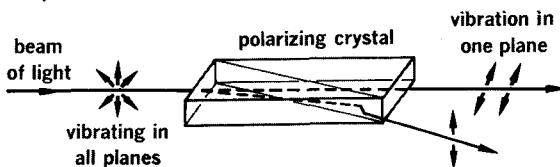


FIG. 28-3

When two calcite crystals are cut along the diagonals and joined as shown, the polarizing crystal thus formed has the property of separating one polarized ray from the other.

When a beam of polarized light is passed through a solution containing one of the isomeric lactic acids, the plane of polarization is rotated in a definite direction and by a definite amount (Fig. 28-4). When the beam is passed through a solution of the other isomer at the same concentration, the plane of polarization is rotated by the same amount but in the opposite direction. The isomer that rotates light to the right (clockwise) is called the *dextro*-form; the one that rotates it to the left (counterclockwise) is called the *levo*-form. A mixture of the two in equal proportions is optically inactive.

**NUMBER OF OPTICAL ISOMERS.** By means of models, it can be shown that the number of optical isomers is  $2^n$ , where  $n$  is the number of unlike asymmetric carbon atoms in a molecule. If  $n$  is 1, the number

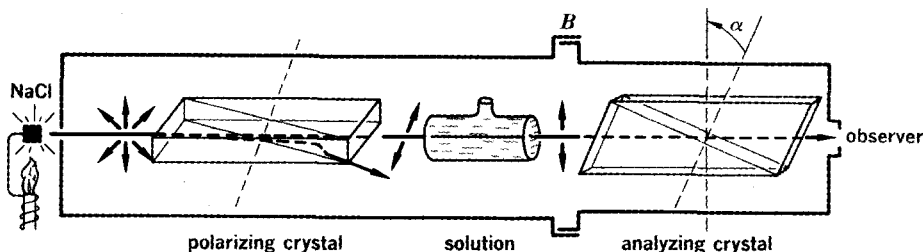


FIG. 28-4

Diagrammatic representation of a polariscope. The part containing the analyzing crystal is joined to the rest of the instrument at *B* so as to permit rotation. The angle of rotation,  $\alpha$ , required to restore the full intensity of the emergent beam measures the rotation produced by the optical isomer in the solution.

of optical isomers is  $2^1$ , or 2; if  $n$  is 2, the number is  $2^2$ , or 4. In the pentose and hexose sugars there are usually 3 or 4 asymmetric carbon atoms per molecule. The number of optical isomers of a given sugar is therefore  $2^3$  (8) or  $2^4$  (16). Note that the optical isomers for a given structural formula can be grouped into pairs, the members of each pair having a mirror-image relationship. Each isomer rotates polarized light, but only the members of a pair rotate it to the same degree but in opposite directions.

**Properties of Optical Isomers.** Any two optical isomers that have a mirror-image relationship are identical in ordinary chemical and physical properties. Separation of a mixture of two such isomers is usually tedious. Two optical isomers that do not have a mirror-image relationship differ in boiling point, melting point, solubility, and certain chemical characteristics, as well as in their action on polarized light. Most of their chemical properties are identical, however, because the same functional groups are present in the molecules of each isomer.

One very important difference in optical isomers of the mirror-image type is their behavior in reactions involving life processes. For example, a given enzyme will catalyze the fermentation of one sugar but not that of its optical isomer. Another example is the adrenal hormone, adrenalin; this hormone is about fifteen times more active in increasing the blood pressure than its mirror-image isomer.

**Historical.** Optical activity was discovered in 1811 by the French chemist Jean Arago. He found that some quartz crystals rotate the plane of polarized light to the right and others to the left. Somewhat later, the physicist Jean Biot found that certain liquids also rotate polarized light. For example, he found that a glucose sugar solution was dextrorotatory and turpentine was levorotatory. In 1844, the great French chemist Louis Pasteur observed that, when a solution

## COMPLEX DERIVATIVES OF HYDROCARBONS

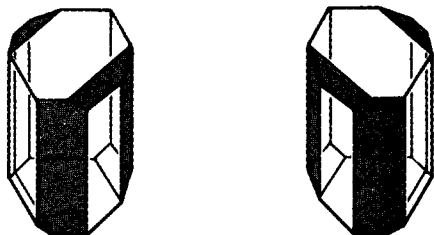


FIG. 28-5

Schematic representation of right- and left-handed crystals of sodium ammonium tartrate.

of sodium ammonium tartrate,  $\text{NaNH}_4\text{C}_4\text{H}_4\text{O}_6$ , was evaporated, crystals were formed, some of which were mirror images of the others (Fig. 28-5). He separated the two by hand-picking and found that a solution of one type rotated polarized light to the right, and the other an equal amount to the left. In 1874, two independent investigators, Jules LeBel and Jacobus Van't Hoff, published papers in which they pointed out that every known optically active organic compound contained at least one carbon atom to which were bonded four different groups. They proposed that, if the four groups were placed at the corners of a tetrahedron, two arrangements in space would be possible and that one would be the mirror image of the other.

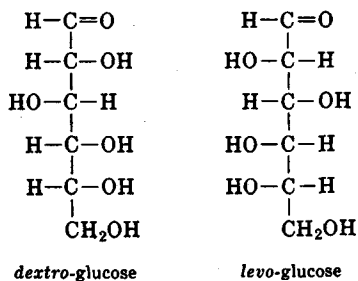
## ISOMERIC ALDOHEXOSES

Because glucose and its fifteen optically active isomers all have an aldehyde group as part of their molecules, they are referred to collectively as the aldohexoses. A study of their molecular formula reveals four unlike asymmetric carbon atoms, as marked in the following formula with asterisks:

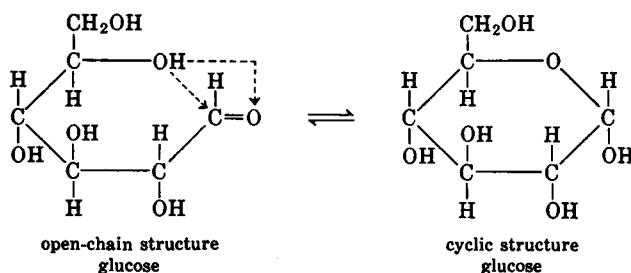


The number of optical isomers predicted is  $2^4$  or 16. These 16 sugars, the aldohexoses, have all been isolated and identified. They are the *dextro*- and *levo*- forms of glucose, mannose, galactose, and five other simple sugars.

Determining the spatial arrangement of the four groups about each asymmetric carbon is a complex process that will not be discussed here. However, the spatial formulas for *dextro*-glucose (common glucose) and its mirror-image isomer, *levo*-glucose, are as follows:

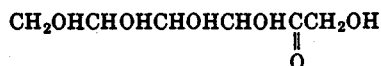


Glucose molecules are now believed to exist mostly in a closed-chain or cyclic form. It will be remembered that the valence angles between carbon atoms are  $109^{\circ}28'$ , rather than the  $180^{\circ}$  angles that our structural formulas would seem to indicate. This means that the aldehyde group on the no. 1 carbon atom can be very close to the hydroxyl group on the no. 5 carbon atom if the chain twists around on itself. The aldehyde and hydroxyl parts can enter into an addition reaction with each other (dotted arrows in formula below) to form a cyclic molecule:



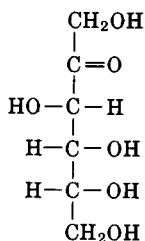
Formation of this ring changes the carbon atom of the aldehyde group to an asymmetric carbon atom. Postulation of this additional asymmetric carbon is necessary to account for the pair of optical isomers that can be derived from *dextro*-glucose. The existence of these isomers is the chief evidence in support of the ring structure. However, the open-chain structure cannot be completely abandoned, because glucose acts as an aldehyde in many of its reactions. Therefore an equilibrium between open-chain and ring molecules is proposed, with perhaps a majority of the molecules being in the closed structure at any one time.

**Fructose.** Fructose,  $C_6H_{12}O_6$  (levulose, fruit sugar), is a crystalline sugar that occurs with glucose in honey and in fruits. Fructose differs structurally from glucose in that it is a ketone type of sugar rather than an aldehyde type. For this reason it is referred to as a *keto*hexose. The open-chain structural formula is

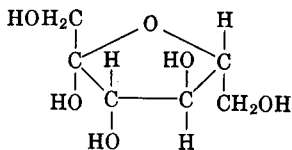


Because there are three asymmetric carbon atoms, there are eight ketohexoses ( $2^3$ ) that have this structure; they differ from one another only in the spatial arrangement of the atoms. The spatial formulas (open and cyclic) for ordinary fructose, one of the eight, are

## COMPLEX DERIVATIVES OF HYDROCARBONS



*levo*-fructose  
(open-chain)

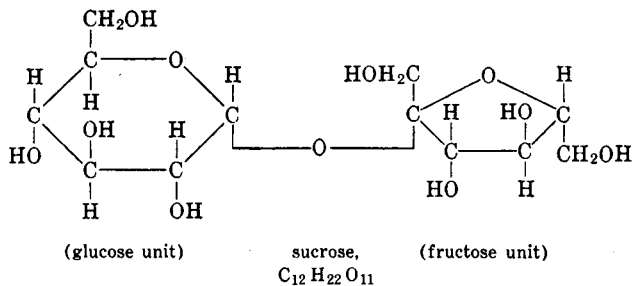


*levo*-fructose  
(cyclic)

Both fructose and glucose are energy foods that are ultimately oxidized to carbon dioxide and water in the cells. However, as might be expected on the basis of their different structures, research indicates that the enzymes and hormones that control these oxidations may be different.

## DISACCHARIDES

Sucrose (table sugar), maltose (malt sugar), and lactose (milk sugar) are important members of the disaccharide group,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ . As the group name indicates, each molecule of these sugars is composed of two monosaccharide units. The units are joined together through bonds that result from the elimination of a molecule of water. For example, a sucrose molecule is composed of a glucose and a fructose unit joined, as shown below:



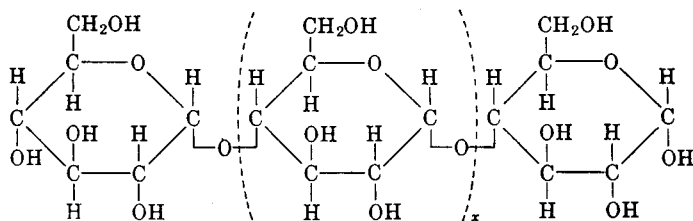
A lactose molecule is also made up of two hexoses: a glucose unit and a galactose unit. Molecules of maltose are built up only of glucose units.

## POLYSACCHARIDES

As the name indicates, molecules of polysaccharides are composed of many monosaccharide units. If the monosaccharide units are pentose sugars,  $\text{C}_5\text{H}_{10}\text{O}_5$ , the polysaccharide is classed as a *pentosan*,  $(\text{C}_5\text{H}_8\text{O}_4)_x$ . If the monosaccharide unit is a hexose sugar,  $\text{C}_6\text{H}_{12}\text{O}_6$ , the polysaccharide is classed as a *hexosan*,  $(\text{C}_6\text{H}_{10}\text{O}_5)_x$ .

Pentosans make up a sizeable portion of corncobs, oat hulls, and similar woody tissues of plants.

**Hexosans.** The most abundant of the hexosan type of polysaccharide,  $(C_6H_{10}O_5)_x$ , are those in which the hexose unit is glucose. *Starch* and *cellulose* are in this group. The manner in which the glucose units are joined in starch molecules is as follows:

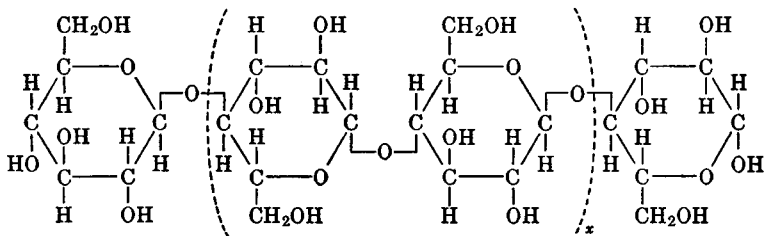


starch

Molecular-weight determinations show that starch molecules contain from 200 to 3,000 glucose units per molecule. The weight of cellulose molecules is more difficult to ascertain. However, the best estimates indicate that the number of glucose units per molecule is of the order of several thousand.

There are at least two important differences in the structure of starch and cellulose molecules. In cellulose, the glucose units are attached end-to-end to form long, filamentlike molecules. In starch, these units are generally joined in a branched-chain pattern, although the smaller unbranched molecules are present in varying amounts in most starches. For example, starch from potatoes contains about 20 per cent of the unbranched type.

A second difference in the structure of starch and cellulose molecules concerns the spatial arrangement of the groups around the two asymmetric carbons by which two glucose units are joined. If we think of the arrangement around these carbons in starch as being "right-handed," the arrangement around the same carbons in cellulose is then "left-handed." A comparison of the formula below for cellulose with the one given above for starch will illustrate this relationship:



cellulose



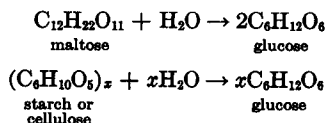
Although this difference may appear trivial, it seems to be related to the fact that man cannot digest cellulose but can digest starch. That is, the enzyme molecules can "fit" the right-handed reactive centers of starch molecules and thereby catalyze the hydrolysis of these large molecules into glucose, but the same enzymes cannot fit into the left-handed centers of the cellulose molecules properly so as to catalyze their hydrolysis.

**OCCURRENCE OF STARCH AND CELLULOSE.** Starch is found in almost all plants. It is especially abundant in the seeds of common cereals (wheat, rye, oats, rice, and corn), constituting from 60 to 80 per cent of the seed. Seeds from peas and beans are about 50 per cent starch. Unripe fruits, such as bananas and apples, contain large proportions of starch that becomes sugar when the fruit ripens. Grains of sweet corn, however, contain an abundance of sugar when the kernels are immature, and only a little sugar but much starch when the grains are ripe.

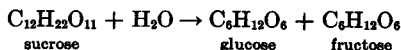
In the plant, the starch molecules are aggregated into larger particles called *granules*. Each species has granules with characteristic shape, size, and markings.

Cellulose occurs in the woody and fibrous parts of plants and is responsible for the structure of plants. Dry wood contains from 60 to 70 per cent of carbohydrate material, about half of which is true cellulose. Cotton is essentially pure cellulose.

**Hydrolysis of Di- and Polysaccharides.** The breaking down (hydrolysis) of complex sugar, starch, and cellulose molecules to monosaccharide molecules is done easily in the laboratory by boiling aqueous solutions or suspensions of the carbohydrate with dilute mineral acids. In the digestive tract of animals, this hydrolysis is effected at body temperature by enzymes that act as catalysts. Maltose, starch, and cellulose form only glucose on complete hydrolysis:



Sucrose yields equal amounts of glucose and fructose:



## COMMERCIAL PRODUCTION OF SUGARS

**Glucose.** Glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , is made by the hydrolysis of starch—usually corn starch in the United States and potato starch in Europe. Water suspensions of the starch are heated in autoclaves with small amounts of hydrochloric acid (0.6 per cent), and hydrolysis is allowed

to take place till a large percentage of the starch has been converted into glucose and the remainder has been hydrolyzed to maltose and to dextrins (soluble starches). The acid present is then neutralized with sodium hydroxide; the sodium chloride thus formed is left in the solution. After decolorizing with charcoal and evaporation of the excess water, a syrup is obtained that is 80 per cent sugar. It is widely used in making candies, chewing gum, and pastries. For table use, some cane syrup may be added to increase the sweetness. The product is sold under a variety of trade names, Karo being one.

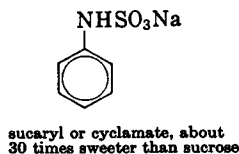
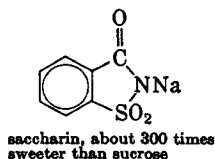
To obtain pure glucose, the hydrolysis of the starch is carried to completion. Neutralization and decolorization, followed by evaporation of the water and removal of the salt, yield the pure, colorless glucose.

**Sucrose.** Sucrose,  $C_{12}H_{22}O_{11}$ , known also as cane sugar and beet sugar, is ordinary table sugar. At present, about two-thirds of our sucrose comes from sugar cane; most of the remainder comes from sugar beets. California and Colorado lead in growing sugar beets, Florida and Louisiana in growing sugar cane. Obtaining pure sugar from these sources involves pressing out the juice, precipitating impurities, decolorizing, evaporating the excess water, and crystallizing. Unlike glucose and fructose, sucrose readily crystallizes from concentrated water solutions. Sugar consumption in the United States is now over 100 lb per person per year.

Sucrose is sweeter than glucose but not so sweet as fructose. With sucrose rated as 100, the comparative sweetness of common sugars is:

lactose	16	sucrose	100
maltose	33	invert sugar	130
glucose	74	fructose	173

Several synthetic, noncarbohydrate compounds are now on the market that are considerably sweeter than sucrose. Two examples are



Because these and other synthetic sweeteners have no food value, they are widely used to sweeten foods and drinks of low-calorie content.

Complete hydrolysis of sucrose produces an equimolecular mixture of glucose and fructose. Because sucrose rotates polarized light to the right and the hydrolysis mixture rotates it to the left, the glucose-fructose mixture is called *invert sugar*. This sugar is sweeter than sucrose. Because invert sugar does not crystallize readily, even from concentrated solutions, it is preferable to sucrose for making some candies and jelly.

In jelly making, the fruit acids catalyze the hydrolysis of sucrose to invert sugar. Consequently it is important that all the sugar be added at the beginning. In candy making, buttermilk, vinegar, or cream of tartar is sometimes added to serve as an acid catalyst for the hydrolysis.

**Maltose.** Maltose or malt sugar,  $C_{12}H_{22}O_{11}$ , is made from starch by a hydrolysis that is catalyzed by the enzyme *diastase*. This enzyme, contained in preparations known as *malt*, is formed during the germination of barley seed.

## CELLULOSE PRODUCTS

Cellulose constitutes the woody portion of all plants and is present in all plant cells. In wood itself, the long molecules of cellulose are laid down in parallel rows to form the wood fibers; the fibers are bound together by a sticky organic substance called *lignin*. (Wood also contains about 8 per cent mineral salts; these become the ash when wood is burned.)

**Paper.** In making paper, wood is cut into small pieces and cooked in calcium bisulfite or other chemicals to dissolve the lignin. The cellulose is removed by filtration, is bleached with chlorine or hydrogen peroxide, and is then weighted, sized, and rolled into sheets. In weighting and sizing, such materials as starch, glue, casein, rosin, aluminum silicate, and clay are added. *Glazed* paper is heavily weighted with minerals (for example, barium sulfate) to reduce porosity; paper toweling contains little mineral additives. Filter paper is almost pure cellulose.

A large amount of the newsprint made in this country consists of a blend of ground wood (about 90 per cent) and cellulose. Because the dry weight of wood is less than 50 per cent cellulose, this method of producing paper makes for economical use of wood.

**Rayon.** Most of the rayon produced in the United States is manufactured by the *viscose* process. Pure cellulose is obtained from wood by the process described above, and treated with aqueous sodium hydroxide and carbon disulfide; the syrupy liquid that forms is called viscose. After aging and filtering, the viscose is forced through the tiny holes of a spinneret into a sulfuric acid bath. This precipitates the cellulose as continuous threads that are gathered and twisted into rayon yarn (Fig. 28-6).

**Cellophane** is made by the same process as rayon, except that the precipitated cellulose is passed between a series of rollers to press it into sheets.

**Cellulose Nitrate and Cellulose Acetate.** Each glucose unit in a cellulose molecule contains three hydroxyl groups. When cellulose

Schematic representation  
of the production of rayon.

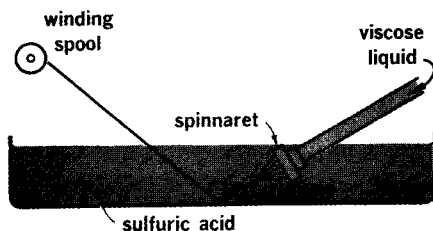


FIG. 28-6

reacts with concentrated nitric acid in the presence of concentrated sulfuric acid, 1, 2, or 3 of these hydroxyl groups are replaced with nitrate groups,  $-\text{ONO}_2$ , forming the ester, *cellulose nitrate*.

If cellulose is treated with acetic acid and sulfuric acid, or with acetic anhydride, the hydroxyl groups are replaced by acetate groups, and *cellulose acetate* is formed. This is used in making acetate rayon and photographic film.

Cellulose nitrate in which a large number of  $-\text{OH}$  groups have been replaced by  $-\text{ONO}_2$  groups is known as *nitrocellulose* or *gun-cotton*. This is an important explosive. Not as violent as nitroglycerin (see page 722), its explosion can take place at a rate suitable for the propulsion of bullets and rockets.

## PROTEINS

Proteins are present in all living tissue, both plant and animal. The tissues of seeds, lean meat, vital organs, skin, and hair contain greater amounts of proteins than do the fatty tissues.

Proteins constitute an important class of foods for animals, because animals cannot synthesize them from the simple inorganic nitrogen compounds, and carbohydrates and fats do not serve as substitutes. Animals are dependent on the plant kingdom for the nitrogen compounds required to build the proteins in muscles, organs, skin, blood, etc.

All protein molecules contain nitrogen in combination with carbon, hydrogen, and oxygen. Many also contain sulfur and phosphorus, and some contain iron, manganese, copper, and iodine. Protein molecules are very large, ranging in molecular weight from about 10,000 awu to several million.

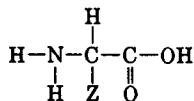
When proteins are boiled in dilute acids or bases or when they are subjected to the action of specific enzymes in digestion, their molecules are hydrolyzed to *amino acids*. Therefore, proteins are like starches and cellulose in the sense that their molecules are built up of repeated units of simpler molecules. The structural units of proteins are amino acids.

## AMINO ACIDS

Amino acids are compounds whose molecules contain both the

## COMPLEX DERIVATIVES OF HYDROCARBONS

amino ( $-\text{NH}_2$ )\* and the carboxyl ( $-\text{COOH}$ ) functional groups. Although hundreds of these acids have been synthesized, only 24 have been obtained by the hydrolysis of proteins. In these the amino group is always attached to the carbon atom adjacent to the carboxyl group:

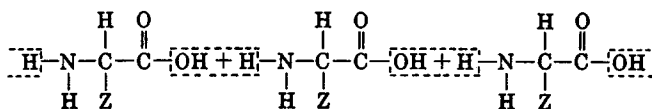


In aminoacetic acid, the simplest amino acid obtained from proteins, Z in the formula above, is hydrogen. In others, Z may be methyl, isopropyl, or butyl, or it may be a carbon chain that also contains sulfur atoms or cyclic groups. The diverse properties of different proteins are accounted for by these variations both in Z and in the size of the protein molecule.

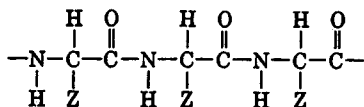
Except in the simplest acid, aminoacetic acid, the carbon attached to the amino group is asymmetric. Such amino acids obtained by the hydrolysis of proteins are therefore optically active.

## STRUCTURE OF PROTEIN MOLECULES

Simple protein molecules are long-chain molecules that are formed by the union of hundreds or even thousands of amino acid molecules. The union is due to valences that can be considered to originate from the elimination of a hydrogen from the  $-\text{NH}_2$  group and an  $-\text{OH}$  from the  $-\text{COOH}$  group. This important linkage is called the peptide bond. The following formulas will help make this point clear:



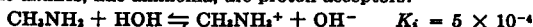
amino acid molecules



portion of protein molecule

**Conjugated Proteins.** Conjugated proteins are made up of simple protein molecules linked to nonprotein molecules. The hemoglobin

\* Three basic groups derived from ammonia,  $-\text{NH}_2$ ,  $=\text{NH}$ , and  $=\text{N}-$ , are often found as components of organic molecules, both synthetic and natural. The simplest compounds containing these groups are the amines,  $\text{RNH}_2$ ,  $\text{R}_2\text{NH}$ , and  $\text{R}_3\text{N}$ , where R is either an alkyl or aryl hydrocarbon radical. Examples are methyl amine,  $\text{CH}_3\text{NH}_2$ ; phenylamine or aniline,  $\text{C}_6\text{H}_5\text{NH}_2$ ; diethyl amine,  $(\text{C}_2\text{H}_5)_2\text{NH}$ ; and trimethyl amine,  $(\text{CH}_3)_3\text{N}$ . The amines, like ammonia, are proton acceptors:



of blood is an example. The protein is combined with *heme*, a complex red compound of iron. Casein in milk and vitellin in egg yolk are also conjugated proteins in which the protein is combined with phosphoric acid. In other conjugated proteins, the additional group may contain carbohydrates, or compounds of nitrogen, magnesium, copper, manganese, cobalt, or other substances.

## POLYMERS

**Polymers** are compounds composed of very large molecules that are formed by the repetitious union of many small molecules. The small molecules, called *monomers*, may be of a single kind, or they may be of several kinds. Cellulose and starch are polymers composed of a single repeating species (glucose units), and proteins are polymers in which the repeating units represent as many as 24 species (amino acid units). As a rule, however, the monomer from which synthetic polymers are formed is of a single type, or at the most, two or three types.

Polymers whose repeating units are bonded by valence bonds made available by the elimination of simple molecules, such as HOH, HCl, and NH<sub>3</sub>, are called *condensation polymers*. Proteins, starch, and cellulose are in this category.

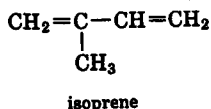
A second kind of polymer is called an *addition polymer*. In this type the repeating units are joined by means of valence bonds associated with unsaturation, for example, double and triple bonds. Polyethylene is classified as an addition polymer.

## RUBBER

Natural rubber is obtained from a rubber tree that grows wild in tropical regions. The world's supply comes mainly from cultivated species of this tree grown in the Far East. When the bark is cut, the tree exudes a milky colloidal dispersion of rubber particles in water. The particles are coagulated as a pasty white material by the addition of an electrolyte, usually acetic acid.

The molecules of rubber are long and chainlike; they are thought to be built up of isoprene units. How these large molecules form in the rubber tree from carbon dioxide and water is unknown.

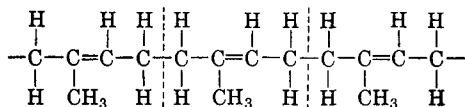
Isoprene itself is a low-boiling colorless liquid whose molecules are of the unsaturated hydrocarbon type:



The polymer obtained by the laboratory polymerization of isoprene is much like natural rubber, and the molecules of each are thought to

## COMPLEX DERIVATIVES OF HYDROCARBONS

be similar, that is, built up of isoprene units in a linear fashion. If a catalyst is used, isoprene undergoes an addition type of polymerization, forming large molecules that contain up to 2,000 isoprene units. In this addition process, the end carbons of the isoprene units become saturated and the middle carbons remain unsaturated. This is shown in the following formula for part of a molecule of rubber:



**VULCANIZATION.** Raw rubber is soft and sticky at room temperature. To be useful, it must be heated with sulfur, a process called **vulcanization**. From 5 to 30 per cent of sulfur is added, depending on the type of rubber desired. Small amounts are used for rubber for soft, easily stretchable articles; larger amounts are used for hard rubber. In vulcanization, the sulfur atoms combine, by addition, with the unsaturated carbon atoms of the rubber molecule. In this addition a sulfur atom may form a bridge between a carbon in one molecule and a carbon in a second molecule. Thus the sulfur atoms link the long-chain molecules together, forming molecules that are large in all three dimensions (see Fig. 28-7).

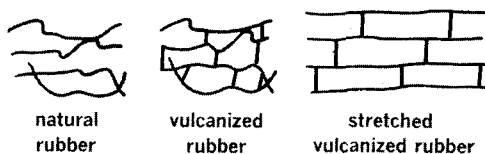


FIG. 28-7

Rubber molecules. (a) In natural rubber, the long molecules are thought to be kinked or coiled and in random orientations; (b) vulcanization produces cross-linking of the molecules; (c) when rubber is stretched, molecules become uncoiled and aligned.

Most rubber articles contain substances other than rubber and sulfur. Black rubber, for example, contains carbon black; red rubber contains antimony sulfide. Such substances are added to increase the strength, resiliency, and durability.

## SYNTHETIC POLYMERS

Natural polymers are not always satisfactory for specific uses. For example, natural rubber swells and loses its elasticity after prolonged exposure to gasoline or motor oil; silk and wool (proteins) are natural foods for certain kinds of bacteria and larvae of insects, as is also cellulose; and most natural polymers are hydrophilic, so that they readily absorb water. Moreover, the stability and melting points of natural polymers are such that they cannot be melted and then cast into desired shapes.

During this century organic chemists have developed hundreds of

synthetic polymers that have specific properties; many can be cast into desired shapes including threads and sheets. In building these polymers, the chemist may choose simple molecules that can unite with one another by the elimination of small molecules, usually water, and form the *condensation type* of polymer; or he may choose unsaturated compounds that can join and form the *addition type* of polymer. Table 28-1 lists a number of common polymers. Note that the first six are of the addition type, the remainder of the condensation type.

A recent development in this field is the discovery of specific catalysts that can link the building blocks into ordered structures rather than random structures. As we have seen, in the natural polymers, such as the proteins, starch, and cellulose, the structural units are always arranged in a particular sequence; and in many instances atoms or groups of atoms are arranged around asymmetric carbon atoms in specific relative positions in space. The fact that variations in positional order can now be achieved with some of the synthetic polymers makes it possible to build, from the same raw materials, polymers that have different properties. Figure 28-8

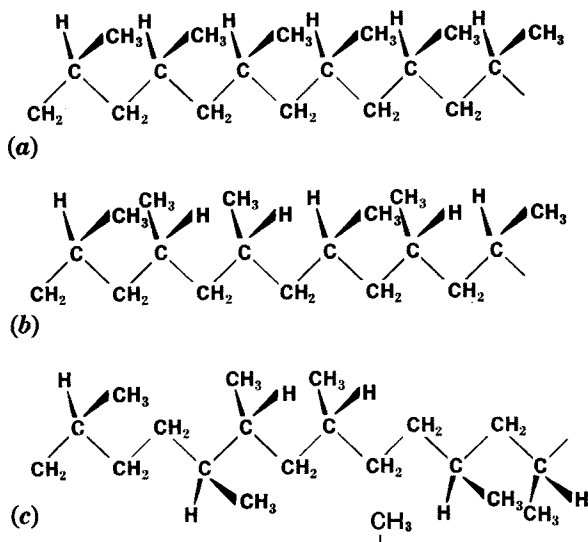




FIG. 28-8

Order and disorder in polypropylene. In (a), the unit  $-\text{CH}-\text{CH}_2-$  is shown joined so that the  $-\text{CH}_3$  group appears always on alternate carbons along the chain. Moreover, the  $-\text{CH}_3$  groups are arranged in space in a regular way. This ordered arrangement allows the molecules to become organized in a regular fashion, and the polymer is said to be crystalline. In (b), the methyl group is also attached to every second carbon, but it occurs at random positions in space. In (c), the methyl groups appear in an irregular sequence along the carbon chain. Too, the polymer has been formed in a way so that the methyl groups appear on first one side of the chain and then on the other.

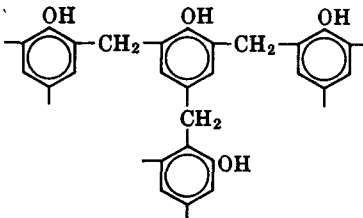


**COMPLEX DERIVATIVES  
OF HYDROCARBONS**

**TABLE 28-1**     *Synthetic polymers*

monomers	polymers	principal uses
$\text{CH}_2=\text{CH}_2$ ethylene	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ polyethylene	films and sheets, tubing, molded objects, electrical insulation
$\text{CH}_2=\text{CHCl}$ vinyl chloride	$-\text{CH}_2\underset{\text{Cl}}{\text{CH}}\text{CH}_2\underset{\text{Cl}}{\text{CH}}-$ polyvinyl chloride	phonograph records, copolymer with vinyl acetate for floor coverings
$\text{CH}_2=\text{CHCN}$ acrylonitrile	$-\text{CH}_2\underset{\text{CN}}{\text{CH}}\text{CH}_2\underset{\text{CN}}{\text{CH}}-$ polyacrylonitrile	fibers, e.g., Acrilan, Orlon
$\text{CF}_2=\text{CF}_2$ tetrafluoroethylene	$-\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2-$ Teflon	objects very resistant to chemical attack
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ butadiene <div> <math>\text{CH}=\text{CH}_2</math>    styrene </div>	$-\text{CH}_2\text{CH}=\text{CHCH}_2\underset{\text{C}_6\text{H}_5}{\text{CH}}\text{CH}_2-$ Buna S and GR-S rubber	synthetic rubber
$\text{CH}_2=\text{CH}\underset{\text{Cl}}{\text{C}}=\text{CH}_2$ chloroprene	$-\text{CH}_2\text{CH}=\underset{\text{Cl}}{\text{C}}\text{CH}_2\text{CH}_2\text{CH}=\underset{\text{Cl}}{\text{C}}\text{CH}_2-$ polychloroprene	oil-resistant rubber, e.g., neoprene
$\text{HOCH}_2\text{CH}_2\text{OH}$ ethylene glycol <div> <math>\text{HO}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{OH}</math>    terephthalic acid </div>	$-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-$ polyethylene terephthalate	fibers, e.g., Dacron; films

*Synthetic polymers (Continued)*

monomers	polymers	principal uses
$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ hexamethylene diamine $\text{HO}-\text{C}(=\text{O})-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(=\text{O})-\text{OH}$ adipic acid	$-\text{NH}-(\text{CH}_2)_6-\text{NH}-\text{C}(=\text{O})-(\text{CH}_2)_4-\text{C}(=\text{O})-$ nylon 66	fibers, molded objects
$\text{C}_6\text{H}_5\text{OH}$ phenol $\text{HCHO}$ formaldehyde	 Bakelite	molded objects, varnishes, lacquers

effect of molecular weight and regularity  
on polypropylene

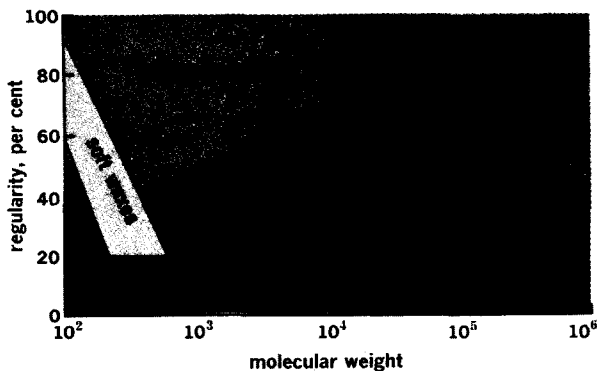


FIG. 28-9

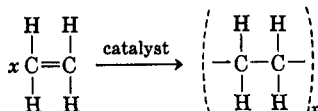
The molecular weight and the regularity of the polymer molecules determine the nature of a plastic material. (Courtesy of Research Laboratories, Tennessee Eastman Co., Division of Eastman Kodak.)

shows the ordered and random molecular structures resulting from the polymerization of propylene,  $\text{CH}_2=\text{CHCH}_3$ . The considerable variation in properties that can be achieved by varying both the structure (as to regularity) and the molecular weight of polypropylene molecules is shown in Fig. 28-9.

**Plastics.** The synthetic polymers shown in Table 28-1 are usually referred to as *plastics*.

From the standpoint of molding, there are two types of plastics: thermoplastics and thermosetting plastics. The *thermoplastics* soften when heated and can be molded repeatedly simply by reheating and then shaping. No chemical change occurs when they are reheated. Cellulose acetate, cellulose nitrate, nylon, and polyethylene are thermoplastics. *Thermosetting plastics* cannot be remolded by heating. To form these in the desired shape, the materials to be polymerized are placed in molds and heated. The substances melt and then undergo polymerization, which often involves cross linking that builds up molecules large in all three dimensions. The polymer then sets to a hard mass in the mold. Bakelite is an example.

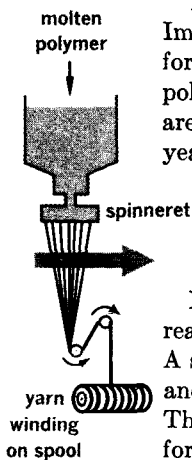
**POLYETHYLENES.** Polymers of ethylene (ethene) are called *polyethylenes*. They are made by the polymerization of ethene under high pressure and in the presence of a catalyst:



The polymerization can be controlled so as to give polymers that are waxlike, or tough and pliable, or hard.

Polyethylenes are *thermoplastic*; that is, they soften and flow on heating and can be cast or extruded in a great variety of shapes which harden on cooling.

The polyethylene type is one of the most useful of all plastics. Important variations can be introduced by substituting other groups for the hydrogen atoms in the ethylene molecule (see the first four polymers in Table 28-1). The polyethylene or *vinyl plastics*, as they are often called, have reached a production of more than 5 billion lb yearly.



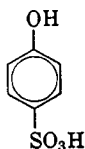
Nylon thread is formed when the molten polymer is extruded through small holes and cooled.

**NYLON.** Nylon is a condensation type of polymer formed by the reaction of adipic acid with hexamethylene diamine (see Table 28-1). A single molecule of nylon contains from 50 to 100 adipic acid units and an equal number of diamine units. Nylon melts at about 265°C. The molten material is extruded through small holes and cooled, forming filaments (Fig. 28-10). The filaments are stretched to make the molecules lie as parallel as possible. Nylon has high tensile strength compared with other fibers, dyes well, and absorbs much less water than silk or wool. For this reason it dries quickly.

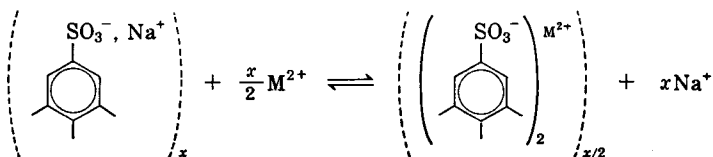
**PHENOL-FORMALDEHYDE PLASTICS (BAKELITE).** When formaldehyde and phenol are heated together in the presence of catalysts, a condensation type of polymerization occurs, forming a resinous material whose structure is shown in Table 28-1.

FIG. 28-10

An interesting and valuable modification of the phenol-formaldehyde polymerization is the use of phenolsulfonic acid



in place of part of the phenol. The resulting polymer contains sulfonic acid groups ( $-\text{SO}_3\text{H}$ ) along the polymer chain and can act as an ion-exchange resin. Its chief use is in the softening of hard water, that is, the removal of ions such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Fe}^{3+}$ . When hard water is passed through a bed of the sodium salt of the ion-exchange resin, the polyvalent metal ions in solution are replaced by  $\text{Na}^+$  ions:



The spent resin is regenerated by allowing it to stand in a concentrated  $\text{NaCl}$  solution.

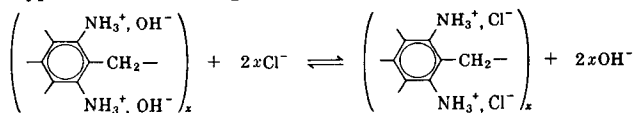
In the acid form, with  $-\text{SO}_3\text{H}$  groups present, the ion-exchange resin can be used to exchange hydrogen ions for metallic ions such as  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , etc. By using it in conjunction with a resin that can exchange  $\text{OH}^-$  ions<sup>1</sup> for negative ions, such as  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Br}^-$ , salts can be removed from water. That is, the  $\text{H}^+$  ion exchanger removes  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , etc., and releases  $\text{H}^+$  ions to the water, while the other removes  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , etc., and releases  $\text{OH}^-$  ions to the water. The  $\text{H}^+$  ions and  $\text{OH}^-$  ions react as they are released to form water (neutralization). Although the process is expensive, it is used to prepare very pure water in the laboratory, and it can be used in emergencies for desalting ocean water.

## CHAPTER REVIEW

### Terms

Carbohydrate, monosaccharide, disaccharide, polysaccharide, pentose, hexose, pentosan, hexosan, asymmetric carbon, optical isomers, plane-polarized light, configurational formula, spatial formula, *dextro*-, *levo*-, *D*-,

<sup>1</sup> One type of  $\text{OH}^-$  ion-exchange material has the following structure:



## COMPLEX DERIVATIVES OF HYDROCARBONS

L-, aldohexose, ketohexose, hydrolysis, synthetic sweetener, cellulose products, protein, amino acid, peptide bond, conjugated protein, polymer, condensation and addition polymers, thermoplastic and thermosetting polymers, order and disorder in polymer molecule, ion exchange resin.

### Exercises

1. You are handed a carbohydrate in the laboratory and told to determine whether it is a monosaccharide. How would you proceed?
2. How could one determine experimentally whether a given sugar is a pentose or a hexose?
3. How many asymmetric carbon atoms are present in a molecule of each of the following:  $\text{CH}_3\text{CHOHCH}_3$ ,  $\text{CH}_2\text{BrCHClCH}_3$ ,  $\text{CH}_3\text{CHOHCHClCOOH}$ ,  $\text{CH}_3\text{CH}_2\text{CHClCHClCHOHCH}_3$ .
4. Refer to Exercise 3. For the compounds containing one or more asymmetric carbon atoms per molecule, calculate the number of possible optical isomers.
5. Refer again to Exercise 3. Write configurational formulas of the type shown in Fig. 28-2 for all possible optical isomers of the compounds listed. You need not designate the *dextro* and *levo* forms, but you should group together pairs that have the object-image relationship.
6. A sucrose solution, when analyzed in a polarimeter, was found to rotate plane-polarized light to the right. The analysis was repeated several weeks later, and the same solution was then found to be *levo*-rotatory. Propose a theory as to what might have happened.
7. Consult the open-chain and closed-chain (cyclic) formulas for glucose. Compare the number of asymmetric carbon atoms in the two structures. Why is it necessary to postulate the cyclic structure?
8. Glucose is sometimes used as the reducing agent in the formation of silver mirrors, that is, to change  $\text{Ag}^+$  to Ag. What happens to the glucose in this process?
9. Write equations for the reactions that occur during the digestion of (a) sucrose, (b) starch, (c) simple proteins, (d) maltose.
10. Outline a method for converting wood into sugar. About what weight of sugar could be obtained from a pound of wood, assuming a 100 per cent yield, based on the amount of cellulose in wood?
11. How are guncotton and acetate rayon related chemically? Compare the combustibility of the two and give a theoretical reason for the difference.
12. In what class of compounds is the peptide bond found? Is this bond subject to cleavage by hydrolysis? Explain.
13. How can the presence of alcohol groups in sugars be proved experimentally?
14. Write the formula for a trisaccharide composed of hexose units. Write the formula for a tetrasaccharide.

15. A new sugar is found to be 40.0 per cent C and 6.67 per cent H by weight. A solution containing 1.05 g of the sugar in 10.0 g of water had a freezing point of  $-0.93^{\circ}\text{C}$ . From these data calculate the molecular formula of the sugar. To what main class and subclass does the sugar probably belong?
16. Which of the following are properly classed as polymers: (a) fats, (b) proteins, (c) sucrose, (d) starch, (e) cellulose nitrate, (f) glyceryl trinitrate, (g) sucrose, (h) ethylene, (i) propylene.
17. Is a "crystalline" polymer crystalline in the same sense that ice is? Explain.
18. Which of the following would probably form polymers under normal reaction conditions for the synthesis of polymers: (a) ethane, (b) ethanol, (c) 1-butene, (d) ethylene glycol,  $\text{HOCH}_2\text{CH}_2\text{OH}$ , (e) a mixture of ethanol and acetic acid, (f) a mixture of glycerol and oxalic acid? For those which probably form polymers, write equations to show the polymerizations. Classify each polymer as to condensation or addition polymer.
19. What is meant by cross-linking? Illustrate.
20. Ocean water contains about 57 lb of gold ions per cubic mile. Would it be feasible to recover the gold by using an ion-exchange resin? Explain why or why not.
21. A polypropylene molecule might weigh as much as 500,000 awu. How many propene molecules would be needed to form such a molecule?
22. Write equations to show how salts can be removed from water by ion-exchange resins.
23. Write equations to illustrate how the following polymers are formed from monomers: (a) Orlon, (b) neoprene, (c) Bakelite, (d) nylon.
24. Natural amino acid molecules have certain features that are usually common to all. Name two such features, and state whether each feature is common to all or to most all. Would it be possible to synthesize amino acids whose molecules do not contain the features just described? Would such amino acids be satisfactory dietary substitutes?
25. A shirt made of ordinary rayon was boiled in dilute hydrochloric acid till it completely dissolved. After filtration to remove buttons, etc., the clear solution was neutralized with sodium hydroxide and then carefully evaporated to dryness. A white solid resulted. What is the probable composition of this solid?
26. Filter paper, on burning, leaves little ash; the paper in this book, if burned, would leave considerable. Why?

### SUPPLEMENTARY READING

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**CHEMICAL****NATURE OF OUR****WORLD**

Chemistry was defined in Chap. 1 as the science that treats of the composition and properties of matter and the changes that matter undergoes. We began our study of the composition of matter with the thesis that the chemical properties of matter could be explained in terms of electrons, protons, and neutrons. In our world, these particles are organized into specific units that form the atoms of more than 100 elements; the atoms of the elements are further organized into molecules and ions of compounds, which make up the great bulk of the nonliving part of our world. In the living part of our world, molecules are further organized, in an exceedingly complex manner, into what might be called the molecule of living matter—the cell. An important conclusion that has been appreciated only recently is that energy plays a dominant role in all these organizations of electrons, protons, and neutrons into the animate and inanimate forms of matter that compose the earth. Indeed, as brought out in Chap. 14, matter and energy are interconvertible.

In the present chapter we shall undertake a brief survey of the gross composition of our planet,<sup>1</sup> and at the same time give attention to a few of the hypotheses with which we seek to account for the organization of the elements and compounds into the structural components of our world. We must realize that not one but many theories have been advanced to explain how our physical world attained its present condition. Two or more hypotheses pertaining to the same single phase often appear equally plausible, and the scientist

<sup>1</sup> The phase of science that is concerned with the chemistry of the earth as a whole is called *geochemistry*; it is a common meeting ground of chemistry and geology.



finds that he does not have enough data, at least for the moment, to help him choose between them. In general, the few hypotheses selected for presentation here have been advanced recently and have been well received by scientists.

## THE UNIVERSE

*Origin.* The solar system, consisting of the sun, the planets and their satellites, the asteroids, the comets, and the meteors, is part of a galaxy that is composed of an estimated 100 billion stars (suns). Farther out in space are a large number of other galaxies of about the same size as ours. These systems of stars are scattered in space at tremendous distances from one another, the nearest one to the earth being about 1 million light-years away.

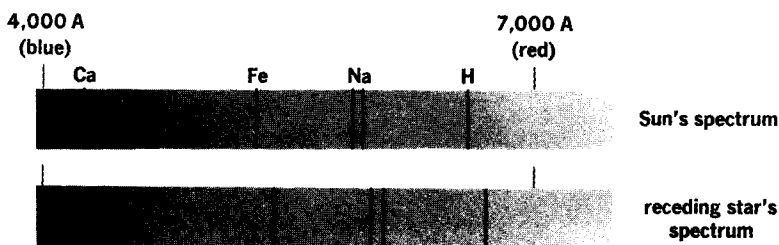


FIG. 29-1

The Doppler effect. Light coming to us from a star moving rapidly away from the earth has a slightly longer wavelength than it would have if the star were moving with the earth. Since all wavelengths are shifted by the same amount, the absorption lines (shown here by dark lines), as well as the continuous background of emitted light (colored portion), are shifted as a group.

Light coming from the distant stars shows a displacement of the spectral lines toward the red portion of the spectrum (the Doppler effect, see Fig. 29-1). This spectral shift is interpreted as meaning that all the galaxies, including our own, are moving outward and away from a common center, the more distant ones moving at greater velocities. This is the concept of the *expanding universe*.

According to one hypothesis that had wide acceptance till recently, all the matter in the known universe, at some time billions of years ago, was located in a comparatively small space under high internal pressure and temperature. With these conditions, elements did not exist; instead, all the matter was in a highly compressed form, consisting perhaps only of neutrons. Presumably, a violent expansion of this primordial matter began, accompanied by cooling as a result of the radiation of energy. The elements then formed from neutrons. (Remember that in certain radioactive changes, a neutron changes into a proton and an electron.) Condensation of the elements around centers of turbulence in the expanding material gave rise to clusters of matter that became stars, planets, etc. All this was supposed to

have happened quite rapidly, perhaps within an hour or so. This theory, often called the *big-bang* theory, was pioneered by the Russian-American physicist George Gamow.

One of the chief supports of the *big-bang* theory, until recently, was that the age of the elements as calculated from isotopic ratios was roughly the same as the calculated time since the chaotic explosion that sent the galaxies rushing apart. The recession velocities, as determined by the spectral red shifts, indicated that about 5 billion years had passed to allow the galaxies to move from a common origin to their present positions.

If it is assumed that the various isotopes of a given element were formed in equal amounts at the beginning of the violent expansion, the age of the elements can be calculated by measuring the relative amounts of radioactive species found remaining today. In the case of uranium, mass spectrographic analyses of ores reveal the relative abundance of the uranium-235 and uranium-238 isotopes to be in a 1:140 ratio. Assuming that the two were formed in equal amounts, the shorter half-life of uranium-235,  $7.1 \times 10^8$  years as compared with  $4.5 \times 10^9$  years for uranium-238, must be responsible for the present ratio of 1:140. Calculations based on these two half-lives of the isotopes give a value of 6 billion years as the time necessary to reduce the proportion of uranium-235 to the present value.

Thus, two entirely different calculations indicated that 5 to 6 billion years had elapsed since the elements formed and the expansion started, and this agreement gave credence to the *big-bang* theory.

Recently, enough evidence has accumulated to cast serious doubt on the *big-bang* theory. Among the new findings are:

1. The compositions of stars differ widely; some are relatively young and are still in the hydrogen fusion process; others are much older, having used all the original hydrogen. These stars probably did not originate at the same time.

2. A redetermination of the time elapsed for the recession, as gauged by the spectral shift, gives a value of about 11 billion years instead of 5 billion years.

According to present-day theories, it is still quite possible that some element building did occur before differentiation into stars and planets occurred. However, it is now believed by many scientists that most of the building of elements occurs in the interior of stars and that this process can account for the natural abundance of nuclides. Other interesting postulates about our universe include (1) the universe is finite; (2) the universe is infinite; (3) matter is being created continuously.

**Composition.** Knowledge of the chemical composition of the universe is obtained by the spectroscopic analysis of light from the stars and planets, and by the analysis of meteorites and earth materials.

It is thought that the earth is not a representative sample of matter,

because it is made from fairly heavy elements, whereas in the universe as a whole hydrogen and helium are by far the most abundant. The stars are the massive heavenly bodies and so account for most of the mass in the universe. Our own star, the sun, is estimated to be about three-fourths hydrogen and one-fourth helium, with traces of many other elements.

## THE EARTH

The planets can be divided into three classes. The small ones nearest the hot sun are composed of substances that condense easily. The second class is made up of substances that can condense if the temperature is low; such planets exist outside the asteroid belt, much farther from the sun than the earth. The third class of planets consists mainly of gases.

Because only a small percentage of the earth (exposed surfaces, drill holes of a depth to about 5 miles, and mines) is available for direct analysis, we do not know much about the total composition of this planet. Data that have been helpful in formulating theories as to the composition of the earth's interior include (1) average density of the earth, (2) composition of meteorites, and (3) seismological data.

**Density of the Earth.** The mass of the earth as calculated from the force of gravity is  $5.98 \times 10^{27}$  g. The volume of a sphere is given by the formula  $4\pi r^3/3$ ; the approximate volume (the earth is not a true sphere) is obtained by substituting its known radius,  $6.37 \times 10^8$  cm, in the formula above and solving. This gives  $1.08 \times 10^{27}$  cc as the volume of the earth. The average density calculated from these data is

$$D = \frac{m}{v} = \frac{5.98 \times 10^{27} \text{ g}}{1.08 \times 10^{27} \text{ cc}} \\ = 5.5 \text{ g/cc}$$

However, the average density of earth material in the accessible crust is only about 2.8 g/cc. We must assume, therefore, in order to account for an overall density of 5.5 g/cc, that matter in the interior has a density that is considerably greater than 2.8 g/cc.

The high density of the earth's interior can be accounted for in two ways: (1) the earth's interior contains a large percentage of dense elements, for example, iron; and (2) gravitational compression of crust material gives rise to greater densities. (See also the footnote to Table 29-1.)

**Composition of Meteorites.** Although the many meteorites that have fallen to the earth vary considerably in composition and type, they may be classified roughly under two headings: (1) the metallic and (2) the stony iron and stone type.

The metallic type consists essentially of a nickel-iron alloy. The

Earthquake waves travel at different velocities through different earth materials. For this reason, the waves are refracted or bent as they pass from one type of material to another. By comparing the time required for shock waves originating at point A to reach recording stations at points B, C, D, etc., around the globe, three major discontinuities and several minor ones have been located.

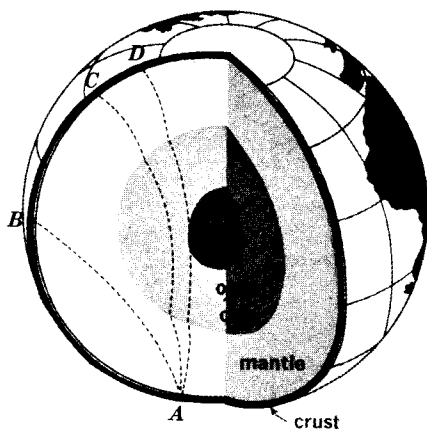


FIG. 29-2

average composition of the alloy, obtained by analyzing many meteors collected around the world, is 90.8 per cent Fe, 8.6 per cent Ni, and 0.6 per cent Co.

The stony iron and stone type consists of about 12 to 50 per cent nickel-iron alloy, the remainder being made up mostly of metallic silicates of such common metals as Fe, Ni, Al, Ca, Na, Mg, Cr, and Mn. Oxides and sulfides may also be present.

Inasmuch as meteorites are thought to represent samples from different depths of one or more planets, their composition has been of great importance in formulating hypotheses as to the nature of the earth's interior. Available information (calculated densities and spectrographic data) indicates that the total composition of different planets varies; consequently too much reliance should not be placed on the composition of meteorites in deducing the composition of the inner portions of the earth.

**Seismological Data.** Earthquake waves travel at varying speeds through the earth, depending on the characteristics of the material through which they pass; hence they are subject to refraction and reflection at the surface of discontinuities. By comparing the time at which the waves from an earthquake arrive at different seismological stations (recorded by an instrument called a *seismograph*), the velocities at different depths can be ascertained (see Fig. 29-2). Such data show clearly that there are three major discontinuities in the earth's interior. The earth is therefore divided into four major parts: the **crust** (lithosphere), which extends down for about 18 to 30 miles to the surface of the first discontinuity; the **mantle**, which extends for about 1,800 miles below the crust; the **outer core**, which extends from the mantle to the inner core, a distance of about 1,300 miles; and the **inner core**, which extends from the outer core to the center, about 4,000 miles from the surface.

TABLE 29-1 *Composition of major zones of the earth*

name	chemical character
atmosphere	N <sub>2</sub> , O <sub>2</sub> , CO <sub>2</sub> , H <sub>2</sub> O, the inert gases, other gases
hydrosphere	salt and fresh water, ice, snow
biosphere	living matter, organic materials
crust (lithosphere)	igneous rocks, shale, sandstone, limestone
mantle	metal silicates, mostly magnesium and iron silicates, with probably considerable metallic sulfides, oxides, etc.
core*	iron-nickel alloy, the outer part probably molten

\* According to one theory, the outer core is liquid and the inner core is solid, both being of the same approximate composition. Recently, consideration of the tremendous pressures that exist at the base of the mantle on through to the earth's center has given rise to a number of new and interesting speculations as to the chemical composition of the core. These pressures, about 1½ million atm at the base of the mantle and about 4 million atm at the center, are believed to cause matter to display properties that are very different from its normal characteristics. Consequently, one hypothesis holds that it is not necessary to consider the core made up of iron and nickel in order to account for the known mass of the earth. Substances of low densities could acquire higher densities under the enormous pressures in the core. Indeed, in 1941 Kuhn and Rittmann of Germany postulated that the earth's core is composed of highly compressed hydrogen. This speculation is contradicted by many arguments. Bullen of Australia considers that the outer core consists of high-density modifications of mantle material and uncombined iron and nickel, and that the inner core is mostly iron and nickel with perhaps some denser materials as well. He argues that this concept makes plausible the view that Mars, Venus, Mercury, and Earth were of the same primitive overall composition.

To complete the major divisions of our planet, three other zones must be added: the **hydrosphere**, the **biosphere**, and the **atmosphere**. Table 29-1 summarizes the chemical character of these zones. The data given there for the composition of the crust, mantle, and core account nicely for the calculated density of the earth and the different velocities of earthquake waves. It is also in accord with the composition of meteorites and with the composition of material brought up from the interior of the earth by volcanic action.

Many scientists think that the earth was formed by gravitational accumulation of cosmic dust. At the same time, other dust eddies condensed to form the sun, moon, and other planets. At the beginning of the formative stage, the temperature was relatively low, but owing to the heat released by the gravitational compression and radioactive changes the earth became molten and remained molten for about 2 billion years, till much of the original radioactive nuclides present had changed to stable nuclides. It is interesting to note that some scientists think that the moon, because it is much smaller than the earth, radiated heat energy more rapidly and, consequently, has never been in the molten form. If this is true, the moon represents an unchanged sample, except for radioactive decay, of the original cosmic dust.

During the molten period, much of the gaseous substances, such as H<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, and the noble gases, escaped from the earth. This assumption is based on the fact that, at the high temperature of the

molten earth, their molecules had sufficient kinetic energy to move out of the earth's gravitational field. The *escape velocity* of a hydrogen molecule is about 7 miles/sec, seven times its speed at sea level at present ordinary temperatures.

The hot molten mass of the young earth was kept in a fairly homogeneous condition by convection currents. The abundant elements were iron, magnesium, silicon, and oxygen, with smaller amounts of calcium, nickel, sodium, and sulfur.

According to one hypothesis, as cooling continued and stable compounds formed, there was not enough oxygen and sulfur to convert all the abundant metals into oxides and sulfides. The excess elemental iron and nickel had higher densities than the compounds and so sank toward the center of the planet, forming the core. The mantle, consisting largely of magnesium and iron silicates, formed a liquid layer around the liquid core. Perhaps a third liquid phase of molten iron sulfide and other metallic sulfides formed as immiscible drops dispersed through the mantle and the core.

It appears likely that all the remaining elements and their compounds became scattered in these three liquid phases, not according to their densities but according to their chemical affinities for either the iron-nickel melt, or the silicate melt, or the metallic sulfide melt. For example, cobalt, the platinum metals, and gold are believed to have concentrated in the core, and uranium and thorium minerals in the crust. As cooling continued, the first substances to become solids were possibly iron and magnesium silicates, members of the *olivine* minerals.<sup>1</sup> Another hypothesis maintains that the first solids were largely metallic oxides and sulfides. All these crystalline compounds are believed to have first formed at the lowermost part of the mantle, thus forming a solid crust around the core that greatly reduced its further cooling. Indeed, the cooling of the core may have been retarded sufficiently so that at least part of it is still in the molten state. The refraction of earthquake waves by the core supports the hypothesis that at least its exterior is liquid.

As crystallization continued in the mantle, the liquid that still remained became enriched with compounds of Al, Ca, Si, O, K, and Na, and, to a lesser extent, compounds of certain other elements. As enrichment continued, these substances formed minerals, such as feldspar and quartz, that accumulated at the top of the molten liquid and eventually aggregated to form a *granitic*<sup>2</sup> type of crust over the mantle.

<sup>1</sup> The olivine minerals crystallize in the orthorhombic system and are orthosilicates of the bivalent metals, such as  $Mg_2SiO_4$  (*forsterite*),  $Fe_2SiO_4$  ( *fayalite*),  $(Mg,Fe)_2SiO_4$  (*olivine*),  $CaMgSiO_4$  (*monticellite*), and  $PbZnSiO_4$  (*larsenite*).

<sup>2</sup> Igneous rocks may be classed as *granitic* or *basaltic*, depending on whether they are acidic or basic. Granitic rocks (granite is a common example) are relatively poorer in the base-forming (metallic) elements and are acidic. Most of the igneous rocks close to the surface are granitic. Both types of igneous rocks contain complex compounds of O, Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, and P, as well as lesser amounts of other elements. Oxygen, aluminum, and silicon usually account for 75 per cent or more of the rock.

# CHEMICAL NATURE OF OUR WORLD

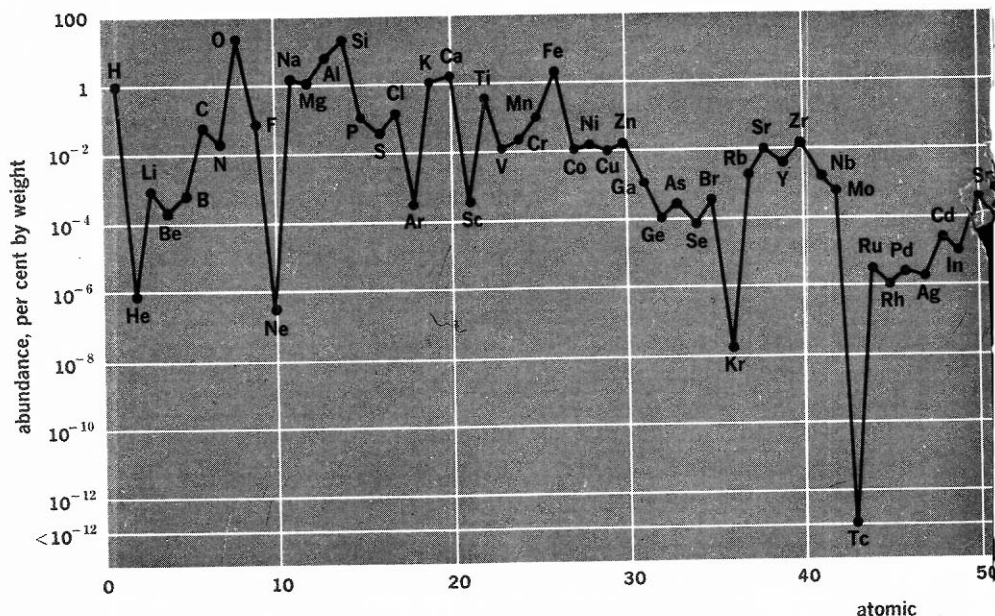


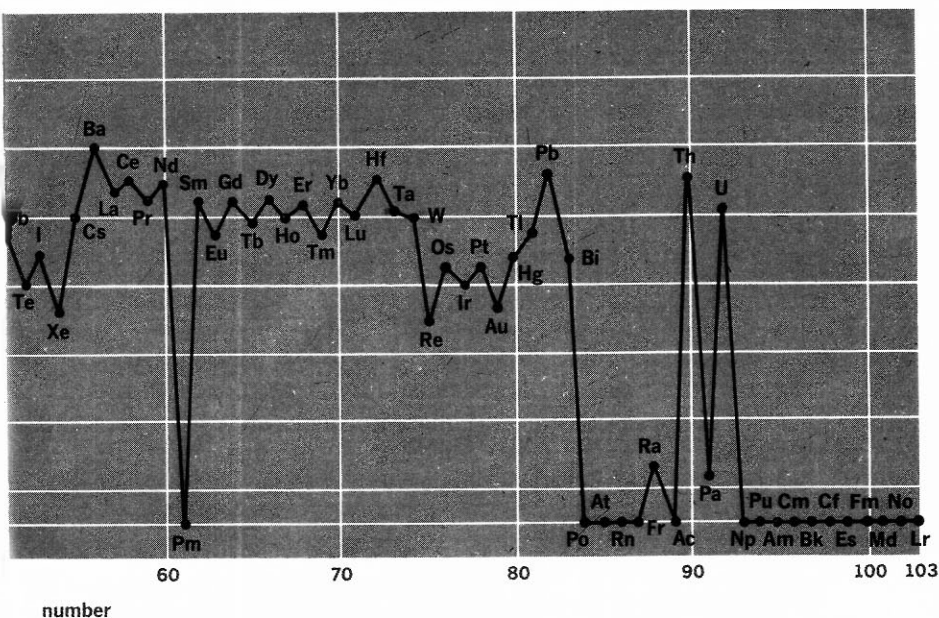
FIG. 29-3

Relative abundances of the elements in the earth's crust. (Data from Michael Fleischer, "The Abundance and Distribution of the Chemical Elements in the Earth's Crust," *J. Chem. Educ.*, **31**: 446 [1954].)

This granitic crust was probably too thin to resist the strong convection currents of the molten layer underneath it; hence it was broken and rebuilt many times. At some later time after it had thickened considerably, it may have been broken again by the currents of the molten mass underneath it, with the parts being folded and piled in a way that formed high and low areas that later became continents and oceans.

The primitive atmosphere was probably composed mostly of carbon dioxide and water. As long as the temperature remained above the critical temperature of water (374°C), water remained as a gas. As the temperature fell, however, vast quantities of water condensed, and the newly formed crust was subjected to considerable chemical and physical erosion.

Clearly, continent-building processes have taken place during the long period of time that has elapsed since the crust finally solidified; otherwise the land would have been leveled to low plains by erosion. Earthquakes, upheavals, and other types of crust movement have continued throughout geologic time. Land at one time under water may now be several thousand feet above sea level, as evidenced by the presence of fossils and other sedimentary materials; or land that at one time must have been above sea level is now under the sea. And these massive displacements in the crust continue today.



Today the uppermost crust of all continental areas is a layer of granitic rock that is usually covered by a relatively thin layer of sedimentary material (soil, limestone, sandstone, etc.) formed by the erosion of the granitic layer. Because the deep parts of the Pacific Ocean have a basaltic bed and because volcanic extrusions are of the basaltic type, it is believed that beneath the granitic layer is a basaltic layer.

## THE CRUST

**Composition.** The upper 10 miles of the crust is estimated to be 95 per cent igneous rocks (rocks formed by the solidification of molten mineral mixtures, for example, granites and basalts), 4 per cent shale, 0.75 per cent sandstone, and 0.25 per cent limestone. In comparison with these, the total amount of other types of sedimentary and metamorphic matter is insignificant. Our knowledge about the average composition of the upper 10 miles of the crust comes from thousands of analyses of minerals and rocks sampled from all parts of the globe.

The percentages by weight of the 12 most abundant elements are shown in Table 29-2. It will be seen from the table that oxygen (combined in such minerals as silicates, carbonates, and oxides) makes up nearly half of the weight of the earth's crust, and that twelve elements (oxygen included) make up 99.5 per cent of the weight.

Figure 29-3 shows the relative abundance in the 10-mile crust of all



*Twelve most abundant elements in the earth's crust  
(per cent by weight)*

TABLE 29-2

oxygen	49.5	calcium	3.4	hydrogen	0.9
silicon	25.7	sodium	2.6	titanium	0.6
aluminum	7.5	potassium	2.4	chlorine	0.2
iron	4.7	magnesium	1.9	phosphorus	0.1
					99.5

the elements up to atomic number 95. Elements with atomic numbers 43, 61, 85, 87, 93, 95, and greater occur in such meager amounts, if at all, that they have never been obtained in reasonably pure form from natural materials. However, studies of radiations emitted from concentrates of natural radioactive materials indicate the presence of very low concentrations of astatine, francium, and some others of the above.

Figure 29-3 reveals that (1) elements with low atomic numbers constitute most of the earth's crust; (2) with some exceptions, elements with even atomic numbers are more abundant than those with odd numbers. Note that an odd-number element is usually less abundant than the two adjacent elements with even numbers. See also Fig. 14-1.

From the standpoint of the second observation, helium, neon, argon, and krypton (even atomic numbers) are much less abundant than would be expected. It is possible that these gases were present in greater quantities early in the earth's history. Great quantities are thought to have escaped from the earth's gravitational field while the planet was in a molten condition. Spectroscopic analyses of light from the sun and other stars indicate a much greater concentration of these elements there than on earth.

Magnesium, chromium, sulfur, selenium, and tellurium (even atomic numbers) also would be expected to be more abundant on the basis of the second observation. These discrepancies may be due to the fact that large amounts of these materials (as sulfides, silicates, and other compounds) sank into the earth's interior while the earth was molten.

*Availability versus Abundance.* It is perhaps surprising to note from Fig. 29-3 that many of the elements that we normally think of as scarce are relatively abundant. For example, platinum is more abundant than silver, and uranium is more abundant than bismuth, mercury, silver, or cadmium. The availability of an element is determined not so much by its relative abundance as by its distribution. If the elements were uniformly distributed in the earth's crust, there would be no search for valuable ores, for one piece of land would be as suitable as the next for ore extraction.

Although the elements may have been uniformly distributed at one

time, many processes have been in operation to bring about the formation of concentrated deposits. It is these concentrated deposits that comprise our workable ores, deposits that are sparsely scattered in the earth's crust.

**Igneous Rocks.** Studies of the crystallization and solidification of molten minerals indicate that, as the molten crust cooled to form igneous rocks, the high-melting oxides of magnesium, iron, and chromium must have crystallized first, forming what is known as the spinel type of mineral; then followed the crystallization of magnesium-iron silicates (olivines) and calcium-sodium-aluminum silicates (feldspars). Possibly, as the first solid compounds formed in the liquid mixture, they sank and formed the deeper rocks, which are low in silicon and rich in magnesium. However, a good deal of the solid material remained suspended; hence when complete solidification occurred, large crystals of the solids formed earlier were embedded in the rock structure that resulted from the solidification of the last liquid portion (see Fig. 29-4).

Three igneous rocks. From left to right: obsidian, granite, and basalt. Note the large crystals embedded in the fine-grained structure of granite and basalt.



FIG. 29-4

The order of these crystallization processes depended not only on the melting points of the minerals, but also on such other factors as ionic radius, ionic charge, and the type of crystalline structures being formed (see Chap. 24). Any ion in a crystal can usually be replaced by another of about the same size without causing serious deformation of the structure. Thus,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Al}^{3+}$  are mutually replaceable in many crystals, as are  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$ . Even ions of the same size but with different charges may replace each other, provided electrical neutrality is maintained by other variations in the crystal. Thus,  $\text{Na}^+$  may substitute for  $\text{Ca}^{2+}$  in feldspars, provided equivalent changes occur in the proportion of  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$ . Compare  $\text{NaAlSi}_3\text{O}_8$  and  $\text{CaAl}_2\text{Si}_2\text{O}_8$  (Table 24-2).

**Sedimentary Rocks.** After the earth's crust solidified, other events brought about further changes in the distribution of the minerals in it. The action of water, wind, carbonic acid, and other agents produced sedimentary material that tended to collect in rivers, lakes, and oceans.

When the sediments were first deposited, they were soft and contained much water. As the amount of sedimentary matter increased,

the lower layers were subjected to pressure that squeezed out most of the water. Minerals that were precipitated from both trapped and seepage water tended to cement the particles together, so that the deposit gradually took on the character of rock. In this manner, such sediments as clay, sand, and lime-mud became shale, sandstone, and limestone, respectively. Rocks of this type, called **sedimentary rocks**, constitute about 5 per cent of the earth's crust.

## THE HYDROSPHERE

The **hydrosphere** includes the oceans, seas, lakes, rivers, underground water, ice, and snow. The oceans and seas form by far the greatest portion of the hydrosphere, perhaps 98 per cent. They cover about 71 per cent of the earth's surface to an average depth of 2.2 miles. This quantity of water and dissolved materials has a volume of about 32 million cubic miles and a weight of about 1,400 million billion tons ( $1.4 \times 10^{18}$  tons).

*Composition of Sea Water.* The relative amounts of the major dissolved minerals in sea water are shown in Table 29-3. Although this table shows only five cations and six anions, ocean water contains traces of essentially all metallic and non-metallic ions.

TABLE 29-3 *Major ionic components of sea water*

cation	per cent	anion	per cent
Na <sup>+</sup>	1.06	Cl <sup>-</sup>	1.90
Mg <sup>2+</sup>	0.13	SO <sub>4</sub> <sup>2-</sup>	0.26
Ca <sup>2+</sup>	0.04	HCO <sub>3</sub> <sup>-</sup>	0.01
K <sup>+</sup>	0.04	Br <sup>-</sup>	0.0065
Sr <sup>2+</sup>	0.01	F <sup>-</sup>	0.0001
		I <sup>-</sup>	0.000005

Vast amounts of minerals are held in solution in the ocean. If all the dissolved minerals in a cubic mile of ocean water were separated by evaporation of the water, the residue would weigh about 140 million (long) tons and would be composed mostly of such compounds as sodium chloride, magnesium sulfate, magnesium chloride, sodium bromide, calcium sulfate, potassium chloride, etc. Complete recovery of certain of the elements in a cubic mile of sea water would yield:

81,000,000 tons of chlorine	200 tons of iodine
43,000,000 tons of sodium	2 tons of uranium
5,600,000 tons of magnesium	57 lb of gold
280,000 tons of bromine	0.5 g of radium

At present only a few substances are produced commercially from sea water.

The major layers of the atmosphere. There is no abrupt change from one layer to the next.

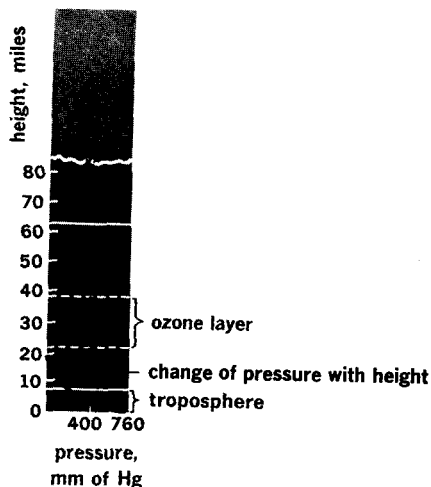


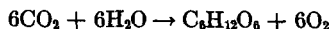
FIG. 29-5

## THE ATMOSPHERE

Figure 29-5 shows the different zones of the atmosphere and the pressure at different heights. It will be noted that atmospheric pressure approaches zero at a height of about 20 miles. The lowest region, the one we live in, is called the **troposphere**; it extends to a height of about 6.5 miles. It is in this region that common atmospheric phenomena, such as cloud formation, air movements, and wide temperature gradations, occur. The next layer is called the **stratosphere**. This region is characterized by the presence of several layers (hence the name) between which there is apparently no strong vertical circulation. Clouds and winds do not exist; it is very cold in the lower strata and warmer in the upper strata. There is a layer of warm ozone, between about 20 and 40 miles, that is due to the action of ultraviolet light on oxygen.

The **ionosphere** is an ionized layer at a fairly high temperature, presumably warmed and ionized by short-wave radiations from the sun. Radio waves are reflected toward the earth by this layer.

**Origin.** It seems highly probable that the atmosphere as we know it today was formed during an extensive period after the earth had cooled sufficiently to permit life. The origin of oxygen has given rise to several controversial theories. According to one hypothesis, most of the oxygen now present in the air is due to *photosynthesis*, a reaction whereby chlorophyll-bearing plants are able to convert carbon dioxide and water into carbohydrates (organic carbon) and oxygen.



If the oxygen of the air was indeed formed by such a process, the

weight of the total amount of this oxygen should bear a definite relationship to the total amount of organic carbon. As indicated by the equation above, the oxygen-to-carbon ratio is 2:1 with respect to atoms, or 32:12 with respect to weight. The organic carbon has largely accumulated as coal and to a lesser extent as petroleum. A small amount is present in the now existing living matter. Although it is difficult to approximate the weights of such huge quantities of matter, the best estimates indicate that the amounts of atmospheric oxygen and organic carbon are in about the ratio that would be expected on the assumption that both were formed by the photochemical process. Note that we need not consider the organic matter that decayed instead of becoming coal, because decay involves the removal of oxygen and the formation of carbon dioxide and water.

The presence of the other components can be accounted for in part as follows. *Gases* trapped in igneous rock were released later by volcanic activity. For example, igneous rocks are known to contain about fifty times as much *nitrogen* as is present in the atmosphere. *Helium* was produced by the radioactive decay of uranium and thorium minerals. *Argon* was produced by the decay of radioactive potassium.

It must be remembered that the theories regarding the earth's origin are quite speculative and that scientists are not in universal agreement on all the various points. Even though each point is based on observable evidence, in many cases the evidence is of such a nature that it can be interpreted equally as well by different theories.

**Composition of Dry Air.** The composition of dry air is given in Table 29-4. Inspection of this table reveals that three gases—nitrogen, oxygen, and argon—make up 99.97 per cent of dry air. Water vapor is not included, because the amount varies widely from day to day and season to season. If water vapor is neglected, the composition of the air is remarkably constant from place to place around the globe. In this respect, dry air resembles a compound. However, the fact that it is a mixture is proved by the following observations:

1. Liquid air has no definite boiling point, as pure compounds do.

TABLE 29-4    *Average composition of dry air*

gas	formula	per cent by volume
nitrogen	N <sub>2</sub>	78.09
oxygen	O <sub>2</sub>	20.95
argon	Ar	0.93
carbon dioxide	CO <sub>2</sub>	0.03
neon	Ne	0.002
helium	He	0.0005
methane	CH <sub>4</sub>	0.0002
traces of krypton, nitrous oxide, hydrogen, xenon, and ozone		

Rather, it boils over a range of temperature (thereby affording a method of separation by mechanical means).

2. Air has no unique properties. Instead, its properties are largely those of a mixture of oxygen, nitrogen, carbon dioxide, and water vapor. If these components were chemically united, their properties would no longer be evident.

The constancy of the composition of the air can be accounted for in two ways: (1) because of the large amount of air and its constant stirring by winds, localized chemical and physical processes that tend to use up one or more components have little effect on the overall composition; (2) oxidation, a major process in the removal of oxygen, is balanced by photosynthesis, a process that restores oxygen.

Our way of life poses the serious problem of air pollution for large cities. It is estimated that the average automobile discharges about 1 lb of contaminants per day into the atmosphere. In a city with 2 million automobiles, this amounts to 1,000 tons per day of such impurities as lead compounds, unburned hydrocarbons, carbon, and other substances ( $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  are excluded). Such contaminants, along with those reaching the air from industrial plants, are a serious menace to the health of the people living in areas thus affected.

Although we may regard the composition of dry air as approximately constant from one place to another, it may be changing slowly with time. At present, the amount of carbon dioxide in the atmosphere is increasing because of man's intense industrial and agricultural activity. The burning of fuels produces  $6 \times 10^9$  tons of this gas per year; destruction of forests in favor of cultivated fields leaves another  $2 \times 10^9$  tons in the atmosphere.<sup>1</sup> These huge amounts are sufficient to displace the equilibria involved in natural processes that maintain a rough balance between the earth and its atmosphere (see Fig. 29-6).

One possible result of this change in the atmosphere is a change in the temperature of the earth. According to one theory, carbon dioxide in the air acts as a blanket to trap heat. The visible radiant energy of the sun comes through the atmosphere efficiently and warms the earth's surface. The earth reradiates much of this energy, but in the infrared rather than in the visible region of the spectrum. Carbon dioxide absorbs infrared radiation efficiently and the radiant heat thus trapped warms the atmosphere and thereby keeps the earth warmer.

According to the data on temperature, the average temperature has increased  $1^\circ\text{F}$  over the past 100 years. This is thought to be due to the  $360 \times 10^9$  tons of carbon dioxide poured into the atmosphere by man's activities in combustion and his destruction of forests. If the present rate of increase in carbon dioxide continues, it is calculated that the temperature will rise another  $2.6^\circ$  by the year 2000. Such differences might result in an appreciable melting of polar ice masses, in cor-

<sup>1</sup> Forests are more efficient in using  $\text{CO}_2$  from the atmosphere than cultivated crops are.

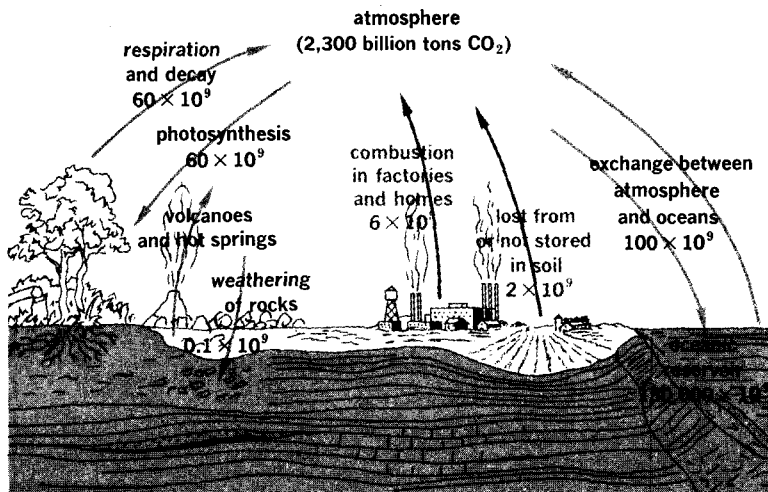


FIG. 29-6

Man's effect (black arrows) on the carbon dioxide cycle.

responding rises in sea levels, and in climatic changes and the accompanying changes in flora and fauna.

**Noble Gases.** The abundance of the noble gases—helium, neon, argon, krypton, and xenon—in the atmosphere is indicated in Table 29-4. (Radon, also one of the noble gases, is radioactive with a very short half-life; it does not occur in detectable amounts in the atmosphere.) The noble gases may be obtained by careful fractional distillation of liquid air. However, because helium, krypton, and xenon are so extremely scarce in the air, they cannot be obtained in appreciable amounts by this process.

Helium is found in fairly high concentrations in certain natural gases, largely from wells in Kansas and Texas. The U.S. Bureau of Mines for several years has been recovering helium from natural gas and storing it against future use. Till recently, this source provided an adequate supply of the element for the few commercial uses which had developed for it. After World War II, the use of helium in atomic energy<sup>1</sup> and missile programs, as well as in certain industrial processes, brought about a sharp increase in the consumption of the element. The Bureau of Mines, to support its helium conservation program, recently increased its recovery facilities and drastically raised the price of the gas (to \$35/1,000 ft<sup>3</sup>).

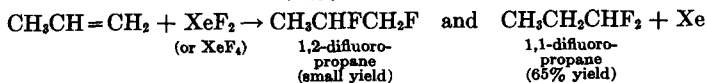
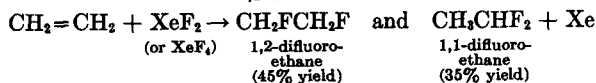
Argon, making up about 1 per cent of the atmosphere, has been steadily increasing in industrial importance and is now being produced to the extent of about 1 billion ft<sup>3</sup> annually. Argon can be used interchangeably with helium in many processes. Welding of titanium

<sup>1</sup> For example, helium serves as the coolant for one type of nuclear reactor operated by the Tennessee Valley Authority for the Atomic Energy Commission.

and other exotic metals in aircraft and rocket construction requires an inert atmosphere, and argon serves this purpose. It is also used in filling incandescent light bulbs, because it does not react with the white-hot tungsten wire as oxygen or nitrogen does. Neon, helium, and argon are used in "neon signs."

Till 1962, it had been assumed that the noble gases, then called the inert gases, would not form compounds. This lack of chemical reactivity was associated with the filled outer shell of electrons, eight for all except helium. In 1962, Neil Bartlett reported the synthesis of the first noble gas compound, xenon hexafluoroplatinate,  $\text{XePtF}_6$ . Since that time several binary compounds of xenon, krypton, and radon have been prepared. These include fluorides and oxides, such as  $\text{XeF}_2$ ,  $\text{XeF}_4$ ,  $\text{XeF}_6$ ,  $\text{XeO}_3$ ,  $\text{KrF}_4$ , and  $\text{RnF}_x$ . They are colorless, crystalline solids, and some are quite stable at room temperature, although others are not. Xenon trioxide, for example, explodes violently when rubbed, pressed, or gently heated. Because of the short half-life of radioactive radon (3.8 days), the chemistry of radon compounds is difficult to determine.

Since their discovery, the main interest in the noble gas compounds has been associated with the fact that they could be prepared at all. Now it seems likely that they will be of practical value. One type of application that gives promise is in the synthesis of fluorine derivatives of hydrocarbons. The direct addition of fluorine to unsaturated hydrocarbons is difficult to control and frequently results in the cleavage of the carbon chain. A group at the Argonne National Laboratory has found that xenon di- and tetrafluorides react with ethenes to give both the 1,1- and 1,2-difluoro addition compounds. Commonly, additions to ethenes give only the 1,2-addition product. The following equations serve to illustrate these points:



In the case of the reactions involving xenon fluorides, it is thought that the 1, 2-addition product first forms and then rearranges to give the 1,1-isomer.

## THE BIOSPHERE

The biosphere includes all the living matter of the world. Because radiant energy from the sun is required for the growth of plant materials and because plants constitute the food of animals, life is largely restricted to areas where sunlight is available, including the oceans to a certain depth.

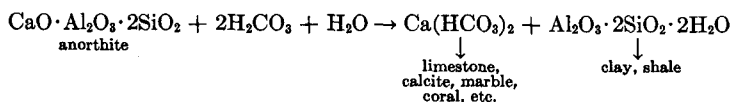


Of the three main areas where there is life—land, fresh water, and sea water—sea water is by far the most important from the standpoint of quantity. It provides approximately three hundred times as much inhabitable space as the other two combined. Estimates of the amount of organic carbon and oxygen produced annually by photosynthesis in different environments (ocean, cultivated land, forests, plains, deserts, etc.), result in the following averages per square mile: land, 62 tons; ocean, 132 tons. These figures lead to the interesting conclusion that, per square mile, the ocean is over twice as productive as the land is. Because the oceans make up about three-fourths of the earth's surface, most of our planet's oxygen is produced in it, as well as most of the organic matter. The oceans are becoming more and more important as a source of food for the world's increasing population.

The great bulk of life in the oceans consists of small organisms, the phytoplankton and the zooplankton. These are found in all oceans from the surface as far down as there is effective light penetration (from 150 to 500 ft).

**Tillable Soil.** Life on the land is directly or indirectly dependent on the thin layer of small rock particles, sand, clay minerals, and decaying organic matter that we call the soil. Good soil must be of the proper texture so that roots, air, and water can penetrate it. It must retain water and plant nutrients, and it must not harden excessively during dry seasons. The formation of such soil requires a very long time, a fact that every progressive farmer appreciates. However, in spite of our best efforts at conservation, large quantities of cultivated soil are lost annually by the action of water and winds.

Soil is formed from rocks by the mechanical action of winds, water, and other agents, and the chemical action of such substances as oxygen, water, and carbonic acid. To illustrate the chemical action of water and carbonic acid, we shall use the chemical reaction that may have occurred when one of the feldspars (anorthite,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) was attacked by these two agents and formed water-soluble or colloidal substances that eventually became limestone, clay, etc.:



Physical changes are important, too, in making rock surfaces available for chemical action. For example, mica (see Table 24-2 and Fig. 24-10) is a potential source of potassium ions, one of the primary plant foods necessary in fertile soil. Normally tightly held between sheets of silicate tetrahedra in mica, potassium ions are exposed and made available for ion exchange when the mica sheets weather, develop cracks, then roll back and flake as the sheets separate. Reactions such as this produce water-soluble compounds of calcium,

sodium, potassium, magnesium, and phosphorus, among others, that can be used by growing plants.

The accumulation of decaying organic matter (humus) in the soil not only returns to it the elements in plant and animal materials but also improves its texture and thus increases its value as a medium for plant growth.

## FORECAST

There are few more appropriate places to look ahead than in the final paragraphs of an introductory text. In chemistry, zoology, psychology, history, or art, if an introduction to the subject is successful, it is but a prelude to one's fuller appreciation of experiences that lie ahead. Whether one plans to take further formal science courses or not, a familiarity with chemistry will enrich the intellectual enjoyment of future studies of all sorts. Hopefully, it will enable one better to discharge his obligations as a citizen in our science-oriented society and to contribute to the discussion of community problems that have technical overtones. Irrespective of one's position on such questions as the fluoridation of water, the hazards of smoking, or the use of pesticides, experience with scientific procedures will help one weigh the evidence presented.

The far-reaching effects of man's unending search for understanding can be illustrated in many fields. Ideally, a study of chemistry will have given each of us, whether prospective scientist or not, a further insight into scientific methods generally. In this text we have had an introduction to the development of chemistry from the time, only about two centuries ago, when the scientific aspects of the subject were the concern of but a few scholars to the present time when the efforts of thousands of scientists are bringing about rapid changes in our way of life. The growing power that man has for scientifically molding his world is awesome, particularly when we reflect that along with desired changes there are problems of misuse or pollution. Medicines, fibers, fuels, foods—even these necessities are being changed as the results of fundamental research quickly affect commerce and industry. It is the proper concern of every educated citizen to evaluate the effects of these changes and to do his part to ensure that new knowledge is used constructively.

For those who look forward to technical careers, there is the exciting prospect of having a part in future developments. To predict is uncertain, but the record of the recent past leads us to believe that undreamt of discoveries lie just ahead. Lavoisier, Dalton, Mendeleev, Kekulé, Pasteur, Rutherford, Haber, Fermi—the successors who will continue their tradition are students today. A large part of the excitement of the search for knowledge is its uncertainty; even the giants of the past and those at work today can only suggest avenues to be explored, and they can be mistaken. Mendeleev did not think

the study of the electron would contribute much to the understanding of atoms of elements, and Rutherford doubted that the great energy of nuclear changes could be usefully harnessed. To take part in the next searches, to make and test the next predictions, or to design useful applications of new discoveries are some of the challenges for those entering careers in science.

## CHAPTER REVIEW

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### *Terms*

Expanding universe, Doppler effect, big-bang theory, age of universe, density of earth, seismograph, meteorite, major zones of earth, mantle, core, crust, biosphere, hydrosphere, atmosphere, igneous rock, sedimentary rock, olivine mineral, granitic, basaltic, troposphere, stratosphere, ionosphere, photosynthesis, noble gases, carbon dioxide cycle.

### *Exercises*

1. What would be true of the translational motion of a star, relative to the earth's, if the spectral lines of light reaching us from the star were shifted toward the blue end of the spectrum; if shifted toward the red; if not shifted at all?
2. In general, how is the composition of a star determined?
3. What kind of data are needed to calculate the rate a given star is receding from the earth?
4. Outline Gamow's theory of the origin of the universe. What are some objections to this theory?
5. The sun has a radius of  $6.96 \times 10^8$  m and a mass of  $1.99 \times 10^{30}$  kg. Calculate its density in grams per milliliter.
6. Some stars contain more heavy elements and less hydrogen and helium than the sun. How has this probably been brought about?
7. According to one theory, the earth formed from solid material and then melted. What could have caused it to melt?
8. The manner in which earthquake waves pass through the earth indicates several discontinuities. What is the meaning here of *discontinuity*? How do earthquake waves reveal them?
9. What evidence indicates that part of the earth's core may be molten?
10. Should the earth's composition from the surface to the center be more or less uniform, because it is supposed to have formed by the solidification of a molten mass? What factors would tend to make the composition uniform? To prevent uniformity?
11. Even though the earth probably was molten at one time, why might some rather dense minerals have concentrated near the surface?

12. Why was the earth's surface probably eroded by water to a greater extent during an earlier period of its history than is happening now?
13. Why are igneous rocks not a satisfactory ore for the recovery of metals such as Al, K, and Na?
14. There are large deposits of rock salt, NaCl, underneath the ground in continental areas, some of which are more than 50 ft thick and cover an area of several square miles. What is probably the origin of these beds?
15. What is the approximate pressure of the atmosphere 10 miles above sea level?
16. Only a relatively small amount of ultraviolet light from the sun penetrates the atmosphere to the earth's surface. Why?
17. What reasons are there for believing that the atmosphere as we know it today was formed over a rather long period after the earth had cooled considerably?
18. Calculate the weight of water vapor in a room 10 ft  $\times$  10 ft  $\times$  10 ft if the temperature is 20°C and the actual vapor pressure of water in the room is 50 per cent of the saturated water vapor pressure.
19. What weight of sea water would have to be processed to obtain 1 ton of magnesium (assume 90 per cent recovery). See Table 30-3.
20. If we assume that the oxygen currently present in the atmosphere was formed by photosynthesis, we must also assume that the plant kingdom developed before the animal kingdom. Why?
21. The amount of carbon dioxide in the atmosphere appears to be slowly increasing. What conditions appear to be responsible?
22. Could it be said that argon is plentiful in nature? Explain.
23. The commercial uses of argon, helium, and neon depend on certain properties of these elements. Are these properties the same for all three, so that the elements can be used interchangeably? Elaborate, citing examples to illustrate your discussion.
24. In which environment is more organic carbon and oxygen produced, land or ocean? Advance a reason as to why one is more productive than the other.
25. The composition of the biosphere is now changing drastically, particularly with respect to man. How is this change in the biosphere affecting the composition of the hydrosphere; the atmosphere; the crust?
26. Rubidium-87 decays to strontium-87, a stable isotope. The half-life is  $4.6 \times 10^{10}$  years. Suppose a meteorite were found in which the  $^{87}\text{Rb}$ : $^{87}\text{Sr}$  is 1:7 by atoms. What is the age of the meteorite? What assumptions are made in this calculation? Would such a find be at variance with the present belief about the age of the universe?
27. On the basis of their ionization energies only, which should be more electronegative, fluorine or argon; fluorine or neon?

28. Write a plausible equation for the explosion of xenon trioxide. Discuss the explosion in terms of hypothetical bond energies.

## SUPPLEMENTARY READING

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## NOTES ON PHOTOGRAPHS

CHAPTER ONE: Etch-pits on cadmium sulfide crystals. (General Motors Research Laboratories.)

CHAPTER TWO: Parabolic mass spectra of various elements. (F. Aston, *Mass Spectra and Isotopes*, 1942. Edward Arnold (Publishers) Ltd. London.)

CHAPTER THREE: Bohr's proposal for the 88 electron "orbits" in a radium atom. (Niels Bohr, *Die Naturwissenschaften*, 1923.)

CHAPTER FOUR: Pyramidal growths of niobium oxide on polished niobium. (J. E. Spruiell, Department of Chemical and Metallurgical Engineering, The University of Tennessee.)

CHAPTER FIVE: Ammonium chloride growth obtained by a freshman student. (Professor Lou Papenhagen, Mount Union College, Alliance, Ohio.)

CHAPTER SIX: Snowflake. (The American Museum of Natural History, New York.)

CHAPTER SEVEN: X-ray diffraction of a single ice crystal. (Photo by I. Fankuchen, *Scientist's Choice*, Basic Books, Inc., Publishers, 1958.)

CHAPTER EIGHT: Hale's pneumatic trough for the collection of gases. (Hales, *Vegetable Statics*, 1727.)

CHAPTER NINE: An analytical balance capable of weighing to 0.000001 g (National Bureau of Standards.)

CHAPTER TEN: Pits etched with acetic acid in a cleaved face of a sodium chloride crystal. (Robert L. Wolfe and C. L. Bauer, *Journal of Applied Physics*, **35**: 660 [1964].)

CHAPTER ELEVEN: Collagen fibrils. (Dr. Jerome Gross, Massachusetts General Hospital. From J. Gross and F. O. Schmitt, *Journal of Experimental Medicine*, **88**, 555, [1948].)

CHAPTER TWELVE: Patterns of copper oxide growing on different crystal faces of a spherical copper crystal. (Professor Allan T. Gwathmey, University of Virginia, From *Advances in Catalysis*, **10**, 64.)

CHAPTER THIRTEEN: Pattern formed by adsorbed droplets of water at imperfections on a  $\text{NiBr}_2$  crystal. (E. N. Sickafus and Dale R. Winder, *Journal of Applied Physics*, **35**: 2542 [1964].)

## NOTES ON PHOTOGRAPHS

CHAPTER FOURTEEN: The decay of a pi-meson. (Brookhaven National Laboratory.)

CHAPTER FIFTEEN: Interior of the "Hilac," a heavy ion linear accelerator. (Courtesy of the University of California Lawrence Radiation Laboratory, Berkeley.)

CHAPTER SIXTEEN: Reaction (in a dark room) of chlorine gas with falling particles of antimony.

CHAPTER SEVENTEEN: Electron diffraction pattern of silicon foils. (W. L. Bell and Professor G. Thomas, College of Engineering and Inorganic Materials Research Division, University of California, Berkeley.)

CHAPTER EIGHTEEN: Magnification of a tiny, tree-like growth of nickel formed during electroplating. (General Motors Research Laboratories.)

CHAPTER NINETEEN: The melting point of gallium is between room and body temperatures. (Aluminum Company of America.)

CHAPTER TWENTY: Bismuth-manganese crystals. (General Electric Research Laboratory.)

CHAPTER TWENTY-ONE: Crystals of sodium chloride. (International Nickel Company, Inc.)

CHAPTER TWENTY-TWO: Crystal of fool's gold,  $\text{FeS}_2$ . (Geology Department, The University of Tennessee.)

CHAPTER TWENTY-THREE: A carbon disulfide suspension of phosphorus is exposed to the atmosphere.

CHAPTER TWENTY-FOUR: Glass etched by  $\text{HF}$  solution plus added ions. (R. M. Tichane and L. B. Wilson, *Journal of Applied Physics*, **35**: 2538 [1964].)

CHAPTER TWENTY-FIVE: A scale model of the benzene molecule.

CHAPTER TWENTY-SIX: Polyether glycol and toluene diisocyanate polymerize to form a polyether foam. (Houdry Process Corporation.)

CHAPTER TWENTY-SEVEN: Fused oxalic acid crystals under polarized light. (General Motors Research Laboratories.)

CHAPTER TWENTY-EIGHT: Rye starch granules; no two plants have identical granules. (Division of Microbiology, DHEW.)

CHAPTER TWENTY-NINE: Glassy, stone tektite (from the moon?) found at Martha's Vineyard. (Division of Meteorites, Smithsonian Institution.)

## ANSWERS TO EXERCISES

*(In working problems, atomic weights are rounded to the nearest tenth of a unit unless the data permit a more precise calculation. Most of these answers are rounded to show the proper number of significant figures.)*

**CHAPTER 1** 3. (a) 6.67 lb; (b) 6.667 lb; (c) 6.7 lb. 6.  $1 \times 10^{-8}$  in.  
7. (a) 10.08 cc; (b) 10.07860 cc. 9. (a)  $-23^{\circ}\text{C}$ ; (b)  $1470^{\circ}\text{F}$ . 10. (a)  $3.8 \times 10^4$  cal; (b)  $2.99 \times 10^5$  cal. 11.  $4.9 \times 10^3$  lb. 13. 2.9 lb Fe.  
14. (b)  $1.2 \times 10^{-25}$  lb/molecule. 17. 0.50 g. 18.  $6 \times 10^4$  gal air.  
19.  $21.5^{\circ}\text{C}$ . 20. 0.796 g/cc. 23. (a) 39.4% Na, 60.6% Cl. 25.  
70.8. 26. 2.92 g.

**CHAPTER 2** 11.  $9 \times 10^{-6}$  erg. 18. 55.84 awu. 27.  $3.4 \times 10^6$  cm/  
sec; 21 miles/sec. 28.  $8.5 \times 10^3$  atoms.

**CHAPTER 3** 7.  $1 \times 10^{15}$  sec $^{-1}$ ;  $3 \times 10^6$  sec $^{-1}$ . 8.  $7 \times 10^{-12}$  erg;  $2 \times 10^{-20}$  erg. 12.  $3 \times 10^{-12}$  erg.

**CHAPTER 4** 2. 61.66%; 60.34%. 25. 1.78 A; 5.08 A.

**CHAPTER 5** 13. (a)  $1.3 \times 10^{23}$  molecules; (b)  $3.1 \times 10^{23}$  atoms; (c)  $6.0 \times 10^{22}$  ions. 14. 70.9 g; 35.5 g; 106.4 g. 15.  $-2.2 \times 10^3$  cal. 16.  
 $-1.2 \times 10^6$  cal/mole. 30.  $1 \times 10^{22}$   $\text{H}_2\text{O}^+$  ions.

**CHAPTER 6** 26.  $5.2 \times 10^4$  cal;  $3.7 \times 10^3$  cal. 27. 1 mole; 18.015 g.  
41. 998 g; 2.20 lb; 55.4 moles.

**CHAPTER 7** 8. 390 mm. 13.  $7052^{\circ}\text{C}$ ;  $-175^{\circ}\text{C}$ . 18. 2.01 A. 19.  
1.13 A. 25.  $156^{\circ}\text{C}$ . 27. 2370 cal/mole; 1430 cal/mole; 560 cal/mole.  
29.  $7.3 \times 10^3$  cal. 30. 724 min. 35. 2.24 g/cc.

**CHAPTER 8** 1. 1,240 mm. 3. 134 ml; 86.3 ml. 4.  $1.3 \times 10^4$  mm.  
6. 280 mm. 8.  $308^{\circ}\text{K}$ ;  $275^{\circ}\text{K}$ ;  $263^{\circ}\text{K}$ ;  $250^{\circ}\text{K}$ . 9. 20.8 liters. 11.  
9.2 atm. 12. 0.25 atm. 14.  $127^{\circ}\text{C}$ . 15. 6.26 liters. 16. (a) 133  
psi; (d) 155 psi. 17. 83.8 ml. 18. 87.0 ml. 19. 0.69 g. 20. 504  
mm. 24. 112 awu; 112 g; 112 g. 25. 98.7 g; 98.7 awu. 26. 750  
mm. 27. 20 g. 29.  $2.60 \times 10^{22}$   $\text{O}_2$  molecules. 30. 56 awu. 32.  
 $7.31 \times 10^{-23}$  g. 34. 8.8 moles; 36.  $r_{\text{CH}_4} = 1.4$   $r_{\text{O}_2}$ . 37. 7.7 atm  
or 110 psi. 40. 0.035 liter; 0.036 liter. 41. 830 mm.



# ANSWERS TO EXERCISES

**CHAPTER 9** 1. (a) 39.3% Na, 60.7% Cl; (d) 28.2% N, 8.1% H, 20.8% P, 42.9% O. 2. 15.8%. 4. 1.25 moles; 17 g; 40 g. 6. 7.9 g. 8. 33.3%. 9. 1.4 g; N<sub>2</sub>, 0.6 g. 10. 0.98 g. 11. 1.0 ton. 13. 0.0213 liter. 14. 80 g. 15. 4.3 g. 16. 0.93 g Mg. 17. Fe, 18.6 g; HNO<sub>3</sub>, 63.0 g. 18. 60.7 g. 19. 32.7 g. 21. 11.1%. 22. 4.9%. 23. CH<sub>2</sub>O. 24. Molecular formula: C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>. 26. 639 awu. 28. 2 liters; 3 liters. 30. CoSO<sub>4</sub>·7H<sub>2</sub>O. 32. C<sub>2</sub>H<sub>6</sub>: 1.34 g/liter; CO: 5.12 g/liter. 33. 66.7%. 34. 0.46 g.

**CHAPTER 10** 12. 36 g. 13. 0.012 mole. 15. 4.8 g; 0.052 mole;  $3.1 \times 10^{22}$  molecules. 16. (a) 63 g; (b) 6.4 N. 17. (a) 320 ml; (b) 0.040 mole. 18. 0.150 M. 19. (a) 1.20 g/ml; (b) 37.5%; (c) 12 M; (d) 16 m; (e) 12 N; (f) 0.23 mole fraction of HCl. 23. 427 ml. 24. 12.2 g/equivalent. 26. 600 ml. 27. 0.119 N. 28. (a) 1.6 m; (b) 0.028 mole fraction; (c) 100.84°C. 29. 12.4°C; 0.2°C. 31. 10°F; -9°F. 32. 78 awu. 33. 16.1 mm. 35. 93 awu. 36. About -1.3°C.

**CHAPTER 11** 1.  $1.5 \times 10^8$  C atoms;  $3.0 \times 10^7$  Al atoms;  $4.2 \times 10^8$  Cs atoms. 24. (a)  $6 \times 10^{10}$  A<sup>3</sup>; (b)  $4 \times 10^9$  atoms. 28.  $1.9 \times 10^4$  cm<sup>3</sup>.

**CHAPTER 12** 3. (a) 0.45 M; (b) 5.0 M; (c) 0.59 M. 5. 597 ml. 13. (a) 8.9; (b) 0.55 mole. 14. 0.26 mole. 16. 4. 19. (a) 0.577 (original  $p_{\text{NO}_2}$ ). 20. 0.2. 32. 0.8 mole/liter. 33. 4. 35. (a) 0.48; (b) 0.37 mole. 37. (a) 3.3 moles; (b) 0.9 mole.

**CHAPTER 13** 7.  $7.0 \times 10^{-5}$ . 8. 4.2%; 35%;  $7.0 \times 10^{-3}\%$ ;  $7.0 \times 10^{-20}\%$ . 15. (a)  $1 \times 10^{-10}$  mole/liter; (b)  $4.3 \times 10^{-6}$  mole/liter. 16. (a)  $1 \times 10^{-11}$  mole/liter; (b)  $1.6 \times 10^{-3}$  mole/liter. 17. (a) 0.70. 18. (a) 0.70; (b) 1.48. 19. (a) 12.38; (b) 1.62; (c) 7; (d) 11.08. 20. 3; 5. 21. 0.06 M acetic acid. 22. 3.1; 2.4; 3.5; 5.2; 6.2. 30. 4.4. 32. 4. 33. (d)  $5.6 \times 10^{-10}$ ; (e)  $7.5 \times 10^{-6}$ ;  $1.3 \times 10^{-9}$ . 34. (a) 5.1; (b) 11.2. 36. (b) KCl:  $1 \times 10^{-7}$ ,  $2.4 \times 10^{-5}$ ; KOH:  $1 \times 10^{-14}$ ,  $2.4 \times 10^{-12}$ . 37. (a) 7; (b) 5.0. 40. 1.9 g/liter; 8.1 g/liter;  $4.7 \times 10^{-8}$  g/liter;  $2.0 \times 10^{-4}$  g/liter. 41. (a)  $1.8 \times 10^{-10}$ ; (b)  $3.5 \times 10^{-11}$ . 42. (a)  $4 \times 10^{-8}$  mole/liter; (b)  $1 \times 10^{-5}$  g/liter.

**CHAPTER 14** 4. (a) 1.57; 1.52; 1.54. 6. (a) beta (1.51); (b) alpha (1.52). 12. (a) 8 alphas, 5 betas; (b) no effect; (c) 14, 18; (d) one. 13. (a) <sup>207</sup>Pb; (b) 3. 16. 0.5 g. 17. 2.5 years. 18. (a)  $6.2 \times 10^{23}$ . 19. (a) 1,700 years. 20. 0.92 curie. 22.  $4.4 \times 10^9$  gal. 28.  $2 \times 10^{-4}$  ppm; 0.0002. 35. 0.1370 awu; exothermic. 36.  $3.34 \times 10^{11}$  cal.

**CHAPTER 15** 3. (a) 0.1510 awu; (b) 1,450 g; (c) 320 lb. 30.  $7 \times 10^9$ .

**CHAPTER 16** 2. 0.6483 kcal/g. 3. (a) 46.96 kcal; (b) -745.6 kcal; (c) -91.11 kcal. 5. (a) 37.3 kcal; (b) 1.4 lb. 6. -1.63 kcal/g. 8. -12.4 kcal/g; -11.9 kcal/g. 10. -184.1 kcal. 12. 21 kcal. 13. -0.6904 kcal/g. 14. (a) -59.5 kcal; (b) -33.1 kcal. 15. 1070 Btu/ft<sup>3</sup>. 17. (b) -46.97 kcal; (c) -127.8 kcal. 18. 2; 24.32 awu. 19. 4; 118.7 awu. 22. (b) +2; TeO; (c) +4; TeO<sub>2</sub>. 24. 60.6 kcal/mole; 50.3 kcal/mole; 110.6 kcal/mole. 25. CH<sub>4</sub>, 100 kcal/mole; CO, 258 kcal/mole. 26. Fluorine:  $1.68 \times 10^{13}$  ergs; 402 kcal. 27. Al<sup>3+</sup>, 1230 kcal/mole. 28. 31 kcal. 29. (a) 64 kcal/mole; (b)  $\pm 8$  kcal/mole. 30. 87 and 79 kcal/mole. 34. 50.3 kcal. 39. (a) -195.50 kcal, yes. 40. 0.0028 kcal/(mole  $\times$  deg). 42. -32.54 kcal; -25.20 kcal; -0.0246 kcal/(mole  $\times$  deg). 45. (a) -12.6 kcal; (b) 13.0 kcal.

**CHAPTER 17** 3. No. 4. Ultraviolet. 12.  $6.2 \times 10^{-5}$  cm. 37. 0.90 Å; yes, Li<sup>+</sup>.

**CHAPTER 18** 1.  $6.24 \times 10^{18}$ . 2.  $7.3 \times 10^{18}$ . 12. (c) 0.57 volt.  
 15. -0.99 volt. 17. (b) 1.38 volts; -0.78 volt; -0.03 volt; 0.01 volt.  
 22. 0.105 g, 1.16 liters  $H_2$ . 23.  $H_2$ , 8 hr 52 min; Au, 8 min 10 sec. 24.  
 0.06099 faraday. 25. (a) 3.7 g; (b) 92%. 26. 29 min. 29. (a)  
 53.2 g; (b) 2; 106.4 awu. 31. 9.4 cents. 38. -80.7. 40. (a) 3.73  
 volts.

**CHAPTER 19** 5. 1.6 times; 4.52 times. 14. (a) 1.13; 1.25. 27.  
 92.8%. 40. (a) 15.63 kcal; -11.3 kcal; 0.0904 kcal/(mole  $\times$  deg); (b)  
 yes.

**CHAPTER 20** 24. 40 Btu/ft<sup>3</sup>. 25. 0.019 ton; 0.037 ton. 34. 2.8  
 cents. 37.  $1 \times 10^{-9}$ .

**CHAPTER 21** 16. (a) 0.5 mole; (b) 2 moles; (c) 1 ft<sup>3</sup>. 20. (a) -8.2  
 kcal; (b) -13 kcal. 22. (a) 12 g; (b) 15 g. 32. (a)  $8 \times 10^7$  Btu;  $2.3 \times$   
 $10^8$  Btu. 41. HF: 17.6 m; 0.241. 42.  $H_2 + I_2 \rightarrow 2HI$ : 16; -7.0 kcal.

**CHAPTER 22** 10. 4.0; 1.8. 13. (a) 25.3 kcal. 19. 4.48 liters.  
 24. 82 lb.

**CHAPTER 23** 24. -76 kcal/mole  $NH_3$ . 27. (b) 50 ft<sup>3</sup>. 42. 83.7 ml.  
 43.  $3.0 \times 10^4$  ft<sup>3</sup>. 46. (a) 9.5 g  $NaH_2PO_4$ , 3.3 g  $Na_2HPO_4$ ; (b) 8.0 g  
 $Na_2HPO_4$ , 7.5 g  $Na_3PO_4$ .

**CHAPTER 24** 16. 15 kcal. 17. 41.2 kcal. 19. 0.33 g. 20. 0.61 g.

**CHAPTER 25** 19. 18 lb  $CO_2$ ; 8.2 lb  $H_2O$ . 23. 37 kcal/mole.

**CHAPTER 26** 6. -372.82 kcal; -337.24 kcal; -310.61 kcal.

**CHAPTER 27** 4. \$88. 15. 3; 5.

**CHAPTER 28** 10. 0.6 lb. 15.  $C_7H_{14}O_7$ .

**CHAPTER 29** 5. 1.41 g/cc. 18. 0.54 lb. 26.  $1.4 \times 10^{11}$  years.

# APPENDIX

## ARITHMETICAL PROCEDURES

### EXPRESSING NUMBERS

Very large numbers and very small numbers are conveniently expressed as powers of 10. This method of expressing numbers is so simple that a few minutes' study will make you sufficiently expert for most purposes. Consider the following:

ordinary number	exponential form
1	$1 \times 10^0$
10	$1 \times 10^1$
100	$1 \times 10^2$
1,000	$1 \times 10^3$
10,000	$1 \times 10^4$
0.1	$1 \times 10^{-1}$
0.01	$1 \times 10^{-2}$
0.001	$1 \times 10^{-3}$
0.0001	$1 \times 10^{-4}$

The number written to the right and above the figure 10 is called an **exponent**. A positive exponent tells how many times a number must be *multiplied* by 10 to give a certain number. Thus,  $1 \times 10^3$  means to multiply 1 by 10 three times, and  $1 \times 10^3$  equals  $1 \times 10 \times 10 \times 10$  equals 1,000. Conversely,  $1 \times 10^{-5}$  means to *divide* 1 by 10 five times. Hence,  $1 \times 10^{-5}$  equals  $1 \div 10 \div 10 \div 10 \div 10 \div 10$  equals 0.00001.

Numbers that are not whole-number powers of 10 are written as follows:

ordinary number	exponential form
200	$2 \times 10^2$
340,000	$3.4 \times 10^5$
0.0000046	$4.6 \times 10^{-6}$

Note that the number to be multiplied by 10 is always between 1 and 10. We write  $2 \times 10^2$ , not  $20 \times 10^1$ ;  $4.6 \times 10^{-6}$ , not  $0.46 \times 10^{-5}$ .

In multiplying numbers expressed as powers of 10, exponents are added; in dividing, exponents are subtracted.

Usual method:

$$300 \times 4,000 = 1,200,000$$

Exponential method:

$$(3 \times 10^2) (4 \times 10^3) = 12 \times 10^5 = 1.2 \times 10^6$$

Two other examples:

$$(7 \times 10^3) (5 \times 10^{-7}) = 35 \times 10^{-4} = 3.5 \times 10^{-3}$$

$$(6 \times 10^4) \div (3 \times 10^5) = 2 \times 10^{-1}$$

Any considerable change in the exponent makes a fantastic change in the size of the number. It has been reliably calculated that there are about  $1 \times 10^{23}$  atoms of copper in three pennies. How many atoms are there in the universe? One times ten to the million? Far from it. It has been estimated that there are  $1 \times 10^{81}$  atoms of matter in the known universe.

Finally, it is sometimes convenient to use the exponent  $-1$  with a unit to denote that the unit is used as a divisor. One can write

$$12 \frac{\text{in.}}{\text{ft}} \quad \text{or} \quad 12 \text{ in. ft}^{-1}$$

$$\text{and} \quad 10 \frac{\text{miles}}{\text{hr}} \quad \text{or} \quad 10 \text{ miles hr}^{-1}$$

Frequency is commonly expressed as  $\text{sec}^{-1}$  (reciprocal seconds):

$$\text{not } \frac{1,470}{\text{sec}} \quad \text{but} \quad 1,470 \text{ sec}^{-1}$$

meaning 1,470 times per second.

## TAKING ROOTS

The use of exponents is often of value in taking roots. Suppose  $x^2 = 159,000$ ; to find  $x$ , we express the number exponentially, taking care to use an exponent that is divisible by two. To do this, we write, not  $1.59 \times 10^5$ , but  $15.9 \times 10^4$ :

$$x^2 = 15.9 \times 10^4$$

$$x = \sqrt{15.9} \times \sqrt{10^4}$$

$$x = 3.99 \times 10^2 = 399$$

Or consider

$$y^2 = 0.000065$$

$$y = \sqrt{65 \times 10^{-6}} = \sqrt{65} \times \sqrt{10^{-6}}$$

$$y = 8.1 \times 10^{-3} = 0.0081$$

Another technique for taking roots is by the use of logarithms. If  $x^2 = 159,000$ ,

$$\log x^2 = 5.2014$$

$$\log x = \frac{5.2014}{2} = 2.6007$$

$$x = \text{antilog } 2.6007 = 399$$

Logarithms are especially valuable for taking roots of high powers. To find  $z$  if  $z^5 = 68.7$ :

$$\log z^5 = 1.8370$$

$$\log z = \frac{1.8370}{5} = 0.3674$$

$$z = \text{antilog } 0.3674 = 2.33$$

Logarithms are easily used in conjunction with exponents. To find  $w$  if  $w^3 = 1.346 \times 10^{-9}$ , first express  $w^3$  as a number in which the 10 has an exponent divisible by 3:

$$w^3 = 134.6 \times 10^{-9}$$

$$w = \sqrt[3]{134.6} \times \sqrt[3]{10^{-9}}$$

Since  $\sqrt[3]{134.6} = \text{antilog of } (\log 134.6)/3 = 5.125$  and since  $\sqrt[3]{10^{-9}} = 10^{-3}$ ,

$$w = 5.125 \times 10^{-3}$$

## SIGNIFICANT FIGURES

In recording a measured or calculated quantity, the number of figures used should indicate the precision with which the quantity is known. Measured quantities that have one uncertain figure may be recorded. Suppose we measure the length of a wooden stick and record it as 121.20 cm. It is understood that the last figure is significant even though it may be somewhat uncertain because of our inability to measure it exactly; we have tried to measure it to the nearest 0.01 cm.

In calculating quantities, the available data may vary in precision; that is, different quantities may have different numbers of significant figures. As an example, consider calculating the volume of a rectangular wooden stick from these measurements: length 121.20 cm., width 3.31 cm., thickness 0.19 cm. In recording these measurements, we imply that in each case the last figure is significant but possibly uncertain. Although we have tried to measure to the nearest 0.01 cm, errors of  $\pm 0.01$  cm may have occurred. By simply multiplying length  $\times$  width  $\times$  thickness ( $L \times W \times T$ ), we calculate the volume to be 76.222680 cc. But to record such a volume would be ridiculous, because it would indicate that we knew the volume precisely to eight significant figures (or to 1 part in over 76 million). Hence we round off the volume to 76 cc. This number has two significant figures, the same number as the least precise of the measurements (the thickness).

*An answer to a multiplication or a division should have the same number of significant figures as there are in the least precise item of data.*

In the volume calculation above, we could have saved time by rounding off the quantities to two significant figures at the outset.

$$L \times W \times T = (1.2 \times 10^2 \text{ cm}) (3.3 \text{ cm}) (0.19 \text{ cm}) \\ = 75.24 \text{ cc} = 75 \text{ cc}$$

This answer indicates 1 part in 76 less than the first answer, but for the purpose of an answer with two significant figures it is fine. (A change of 1 part less in 19 in the thickness would result in an answer which would be even smaller than 75 cc.)

Quantities are often expressed with greater precision than can be justified. The population of a city may be given as 125,762; but 126,000 would probably be sufficiently precise, in view of the uncertainty of the present counting techniques. Whether zeros at the end of a number are considered as significant or not must often be decided on the basis of common sense. If a friend mentions that he has saved \$25 in pennies in his piggy bank, one might think the sum of 2,500 pennies had two or three significant figures. But if one purchased \$25 in pennies from a bank, the sum of 2,500 pennies would be expected to be precise to four figures. A feel for significant figures was not one of the talents of the man who said he had a fossil 3,500,016 years old. This he knew because a geologist had told him it was 3,500,000 years old 16 years ago.

Quantities are often expressed with greater precision than is necessary for a particular problem. Atomic weight, Avogadro's number, solubility, etc., may be known very precisely. Although we sometimes need such precise figures, often we do not. The following example illustrates this point.

A sample of oxygen was found to weigh 1.23 g. Calculate the number of moles of oxygen in the sample. From a handbook, we find that 1 mole of oxygen weighs 31.9988 g. Our problem requires division: grams  $\div$  grams per mole = moles. Before dividing, however, we round the handbook figure to three significant figures, 32.0 grams per mole.

$$\text{no. moles} = \frac{1.23 \text{ g}}{32.0 \text{ g/mole}} = 0.0384 \text{ mole}$$

A little practice will enable you to determine the number of significant figures in different quantities very quickly. The following examples illustrate some typical cases:

quantity	no. of significant figures
1.062 grams	4
751 students	3
0.006110 centimeter	4
$1.2 \times 10^8$ feet	2
7,685,000 people	4
\$683,462.02	8

## FACTOR-UNITS METHOD

To help master units of measurement, it is desirable to set down the units along with the numbers that they qualify, and then multiply and divide these units as indicated in solving the problem. The following problems illustrate the handling of units in calculations.

**PROBLEM 1** Calculate the area of a table that measures 30 in. by 40 in.

$$\begin{aligned}\text{Solution} \quad \text{Area} &= 30 \text{ in.} \times 40 \text{ in.} \\ &= (30 \times 40)(\text{in.} \times \text{in.}) \\ &= 1,200 \text{ in.}^2 \text{ (i.e., inches multiplied by inches, or 1,200 sq in.)}\end{aligned}$$

**PROBLEM 2** Convert 40 in. to yards. Given: 12 in. = 1 ft; 3 ft = 1 yd.

At this point, it is important to fit the term *per* into our mathematical language by noting that *this term implies division*. Thus, 12 in. = 1 ft may be read 12 inches per foot and written  $\frac{12 \text{ in.}}{1 \text{ ft}}$ . Similarly, the relationship

between feet and yards may be written  $\frac{3 \text{ ft}}{1 \text{ yd}}$ . In arithmetical operations, we

may wish to use the reciprocals of these ratios, i.e.,  $\frac{1 \text{ ft}}{12 \text{ in.}}$  and  $\frac{1 \text{ yd}}{3 \text{ ft}}$ , respectively.

Now we set up the ratios or factors so that units cancel to give the conversion of 40 in. to yards.

$$\text{Solution} \quad \text{Length} = 40 \cancel{\text{in.}} \times \frac{1 \cancel{\text{ft}}}{12 \cancel{\text{in.}}} \times \frac{1 \text{ yd}}{3 \cancel{\text{ft}}} = \frac{40 \text{ yd}}{12 \times 3} = 1.1 \text{ yd}$$

**PROBLEM 3** Calculate in square meters the area of a table that measures 30 in. by 40 in. Given: 36 in. = 1 yd; 1 m  $\times$  1.09 yd.

*Solution*

$$\begin{aligned}\text{Area} &= \left( 30 \cancel{\text{in.}} \times \frac{1 \cancel{\text{yd}}}{36 \cancel{\text{in.}}} \times \frac{1 \text{ m}}{1.09 \cancel{\text{yd}}} \right) \times \left( 40 \cancel{\text{in.}} \times \frac{1 \cancel{\text{yd}}}{36 \cancel{\text{in.}}} \times \frac{1 \text{ m}}{1.09 \cancel{\text{yd}}} \right) \\ &= \frac{30 \times 1 \times 1 \text{ m}}{36 \times 1.09} \times \frac{40 \times 1 \times 1 \text{ m}}{36 \times 1.09} \\ &= 0.78 \text{ m}^2 \text{ or sq m}\end{aligned}$$

**PROBLEM 4** Calculate in calories the heat required to raise the temperature of 20 g of water by 10 degrees centigrade. Given: The specific heat of water = 1 calorie per gram per degree,  $\frac{1 \text{ cal}}{1 \text{ g} \times 1 \text{ degree C}}$ ; i.e., 1 calorie is required to raise the temperature of each gram of water by 1 degree centigrade temperature.

$$\begin{aligned}\text{Solution} \quad \text{Calories required} &= \frac{1 \text{ cal}}{1 \cancel{\text{g}} \times 1 \cancel{\text{degree C}}} \times 20 \text{ g} \times 10 \cancel{\text{degrees C}} \\ &= 200 \text{ cal}\end{aligned}$$

Solving problems by setting up factors so that units cancel to give an answer containing the desired unit can be quite helpful. However, this method can also become entirely too mechanical. The problems in this text are useful, not as exercises in arithmetic, but as a means of developing your understanding of chemical methods and principles. Consequently, problem solving should begin with an analysis of the terms and language used in the problem. This analysis should lead to a definite prediction of what the answer will be before any precise calculations are made. In general, then, solving a problem should involve:

1. Analyzing and predicting the approximate magnitude and units of the answer

2. Setting up mathematical equations and carrying out calculations
3. Checking work by canceling units and inspecting the magnitude of the answer

The next two problems and their solutions illustrate this three-step attack.

**PROBLEM 5** When 12 tons of coke is burned to carbon dioxide, 32 tons of oxygen is required. How much oxygen is needed to burn 100 tons of coke?

*Analysis* Since 100 is just over 8 times 12, the amount of oxygen used will be between 8 and 9 times 32 tons, that is, between 256 and 288 tons of oxygen.

*Solution* For purposes of calculation we set up our equation so that the units cancel to give an answer in tons of oxygen:

$$32 \text{ tons of oxygen} \times \frac{100 \text{ ~~tons of coke~~}}{12 \text{ ~~tons of coke~~}} = 267 \text{ tons of oxygen}$$

Since we made a thorough analysis of the problem, we have only to compare this answer with our prediction to see that the answer is reasonable. Such an approach should help in detecting careless mistakes, especially decimal point errors that might lead to such incorrect answers as 26.7 or 2670 tons of oxygen. Note that two of the weights used in the calculation have only two significant figures. Therefore, the answer should be rounded to 270 tons.

**PROBLEM 6** A quantity of gas measures 100 ml at a pressure of 15 psi (lb per sq in.). What is its volume at 25 psi? Given: As the pressure on a gas increases, the volume decreases proportionately.

*Analysis* The volume will be considerably smaller; i.e., the gas will be compressed. However, the volume will not be reduced to one-half its original amount (i.e., to 50 ml) because the pressure has not been doubled.

*Solution*

$$100 \text{ ml} \times \frac{15 \text{ ~~psi~~}}{25 \text{ ~~psi~~}} = 60 \text{ ml}$$



TABLES

TABLE 1      *Conversion factors*

1 lb (avoirdupois) = 453.59 g	1 in. = 2.54 cm
1 oz (avoirdupois) = 28.350 g	1 m = 39.370 in.
1 kg = 2.2046 lb (avoirdupois)	1 angstrom (A) = $1 \times 10^{-8}$ cm
1 liter = 1.0567 qt (U.S.)	1 km = 0.62137 miles
1 gal (U.S.) = 3.7854 liters	1 atm = 760 mm (Hg)
1 cu ft = 28.3 liters	1 atm = 14.7 psi
1 ml = 0.061025 cu in.	$\Delta 1^{\circ}\text{C} = \Delta 1.8^{\circ}\text{F}$
1 ml = 1.000028 cc	1 ev = $1.602 \times 10^{-12}$ erg
1 cu in. = 16.387 ml	1 cal = $4.184 \times 10^7$ ergs
1 cu ft = 28,317 ml	1 Btu = 251.98 cal

Factors that are useful to remember:

1 lb = 454 g      1 in. = 2.54 cm      1 liter = 1.06 qt       $\Delta 1^{\circ}\text{C} = \Delta 1.8^{\circ}\text{F}$

Common prefixes, abbreviations in parentheses:

centi- (c-)	milli- (m-)	micro- ( $\mu$ )	kilo- (k-)
1/100	1/1,000	1/1,000,000	1,000

TABLE 2      *Vapor pressure of water at different temperatures*

temperature, $^{\circ}\text{C}$	vapor pressure, mm of Hg	temperature, $^{\circ}\text{C}$	vapor pressure, mm of Hg
0	4.58	29	30.04
5	6.54	30	31.82
10	9.21	31	33.70
11	9.84	32	35.66
12	10.52	33	37.73
13	11.23	34	39.90
14	11.99	35	42.18
15	12.79	40	55.32
16	13.63	45	71.88
17	14.53	50	92.51
18	15.48	55	118.04
19	16.48	60	149.38
20	17.54	65	187.54
21	18.65	70	233.7
22	19.83	75	289.1
23	21.07	80	355.1
24	22.38	85	433.6
25	23.76	90	525.8
26	25.21	95	633.9
27	26.74	100	760.0
28	28.35	150	3570.5

*Solubility product constants\**

TABLE 3

compound	solubility product constant
arsenic(III) sulfide, $As_2S_3$	$4 \times 10^{-29}$
barium sulfate, $BaSO_4$	$1 \times 10^{-10}$
bismuth sulfide, $Bi_2S_3$	$6.8 \times 10^{-97}$
cadmium sulfide, $CdS$	$7.8 \times 10^{-27}$
calcium carbonate, $CaCO_3$	$1 \times 10^{-8}$
calcium oxalate, $CaC_2O_4$	$1.78 \times 10^{-9}$
calcium sulfate, $CaSO_4$	$2 \times 10^{-4}$
cobalt sulfide, $CoS$	$3 \times 10^{-26}$
copper(II) sulfide, $CuS$	$8.7 \times 10^{-36}$
iron(III) hydroxide, $Fe(OH)_3$	$1 \times 10^{-38}$
lead chloride, $PbCl_2$	$1 \times 10^{-4}$
lead sulfate, $PbSO_4$	$1 \times 10^{-8}$
lead sulfide, $PbS$	$8.4 \times 10^{-28}$
magnesium hydroxide, $Mg(OH)_2$	$1.2 \times 10^{-11}$
manganese sulfide, $MnS$	$1.4 \times 10^{-11}$
mercury(II) sulfide, $HgS$	$3.5 \times 10^{-52}$
nickel sulfide, $NiS$	$1.8 \times 10^{-21}$
silver chloride, $AgCl$	$1 \times 10^{-10}$

\*  $K_{sp}$  varies with temperature. The constants listed were determined at temperatures ranging from 18 to 25°C. For sulfides, see W. H. Waggoner, *J. Chem. Educ.*, **35**: 339 (1958).

*Solubilities of common metal compounds\* in water*

TABLE 4

compound	solubility
acetates	all soluble except $Ag^+$ , $Hg^+$ , $Bi^{3+}$
nitrates	all soluble
nitrites	all soluble except $Ag^+$
chlorides	all soluble except $Ag^+$ , $Hg^+$ , $Pb^{2+}$ , $Cu^+$
bromides	all soluble except $Ag^+$ , $Hg^+$ , $Pb^{2+}$
iodides	all soluble except $Ag^+$ , $Hg^+$ , $Pb^{2+}$ , $Bi^{3+}$
sulfates	all soluble except $Pb^{2+}$ , $Ba^{2+}$ , $Sr^{2+}$
sulfites	all insoluble except $Na^+$ , $K^+$ , $NH_4^+$
sulfides	all insoluble except $Na^+$ , $K^+$ , $NH_4^+$ , $Ba^{2+}$ , $Sr^{2+}$ , $Ca^{2+}$
phosphates	all insoluble except $Na^+$ , $K^+$ , $NH_4^+$
carbonates	all insoluble except $Na^+$ , $K^+$ , $NH_4^+$
oxalates	all insoluble except $Na^+$ , $K^+$ , $NH_4^+$
oxides	all insoluble except $Na^+$ , $K^+$ , $Ba^{2+}$ , $Sr^{2+}$ , $Ca^{2+}$
hydroxides	all insoluble except $Na^+$ , $K^+$ , $NH_4^+$ , $Ba^{2+}$ , $Sr^{2+}$ , $Ca^{2+}$

\* The compounds listed here include only those of the common metals of groups IA, IB, IIA, and IIB, and Mn, Fe, Co, Ni, Al, Sn, Pb, Sb, and Bi. The polyatomic ion  $NH_4^+$  is included because of its importance.

APPENDIX

TABLE 5 *Four-place logarithms*

natural numbers											proportional parts									
	0	1	2	3	4	5	6	7	8	9										
											1	2	3	4	5	6	7	8	9	
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37	
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34	
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31	
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29	
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27	
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25	
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24	
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22	
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21	
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20	
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19	
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18	
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17	
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17	
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16	
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15	
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15	
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14	
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14	
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13	
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13	
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12	
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12	
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12	
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11	
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11	
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11	
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10	
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10	
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10	
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10	
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9	
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9	
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9	
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9	
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9	
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8	
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8	
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8	
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8	
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8	
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8	
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7	
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7	
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7	

## APPENDIX

natural numbers	0 1 2 3 4					5 6 7 8 9					proportional parts									
											1 2 3 4	5 6 7 8 9								
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1 2 2 3	4 5 5 6 7								
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1 2 2 3	4 5 5 6 7								
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1 2 2 3	4 5 5 6 7								
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1 1 2 3	4 4 5 6 7								
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1 1 2 3	4 4 5 6 7								
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1 1 2 3	4 4 5 6 6								
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1 1 2 3	4 4 5 6 6								
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1 1 2 3	3 4 5 6 6								
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1 1 2 3	3 4 5 5 6								
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1 1 2 3	3 4 5 5 6								
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1 1 2 3	3 4 5 5 6								
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1 1 2 3	3 4 5 5 6								
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1 1 2 3	3 4 5 5 6								
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1 1 2 3	3 4 4 5 6								
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1 1 2 2	3 4 4 5 6								
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1 1 2 2	3 4 4 5 6								
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1 1 2 2	3 4 4 5 5								
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1 1 2 2	3 4 4 5 5								
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1 1 2 2	3 4 4 5 5								
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1 1 2 2	3 4 4 5 5								
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1 1 2 2	3 3 4 5 5								
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1 1 2 2	3 3 4 5 5								
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1 1 2 2	3 3 4 4 5								
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1 1 2 2	3 3 4 4 5								
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1 1 2 2	3 3 4 4 5								
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1 1 2 2	3 3 4 4 5								
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1 1 2 2	3 3 4 4 5								
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1 1 2 2	3 3 4 4 5								
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1 1 2 2	3 3 4 4 5								
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1 1 2 2	3 3 4 4 5								
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1 1 2 2	3 3 4 4 5								
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1 1 2 2	3 3 4 4 5								
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0 1 1 2	2 3 3 4 4								
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0 1 1 2	2 3 3 4 4								
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0 1 1 2	2 3 3 4 4								
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0 1 1 2	2 3 3 4 4								
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0 1 1 2	2 3 3 4 4								
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0 1 1 2	2 3 3 4 4								
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0 1 1 2	2 3 3 4 4								
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0 1 1 2	2 3 3 4 4								
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0 1 1 2	2 3 3 4 4								
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0 1 1 2	2 3 3 4 4								
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0 1 1 2	2 3 3 4 4								
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0 1 1 2	2 3 3 4 4								
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0 1 1 2	2 3 3 3 4								



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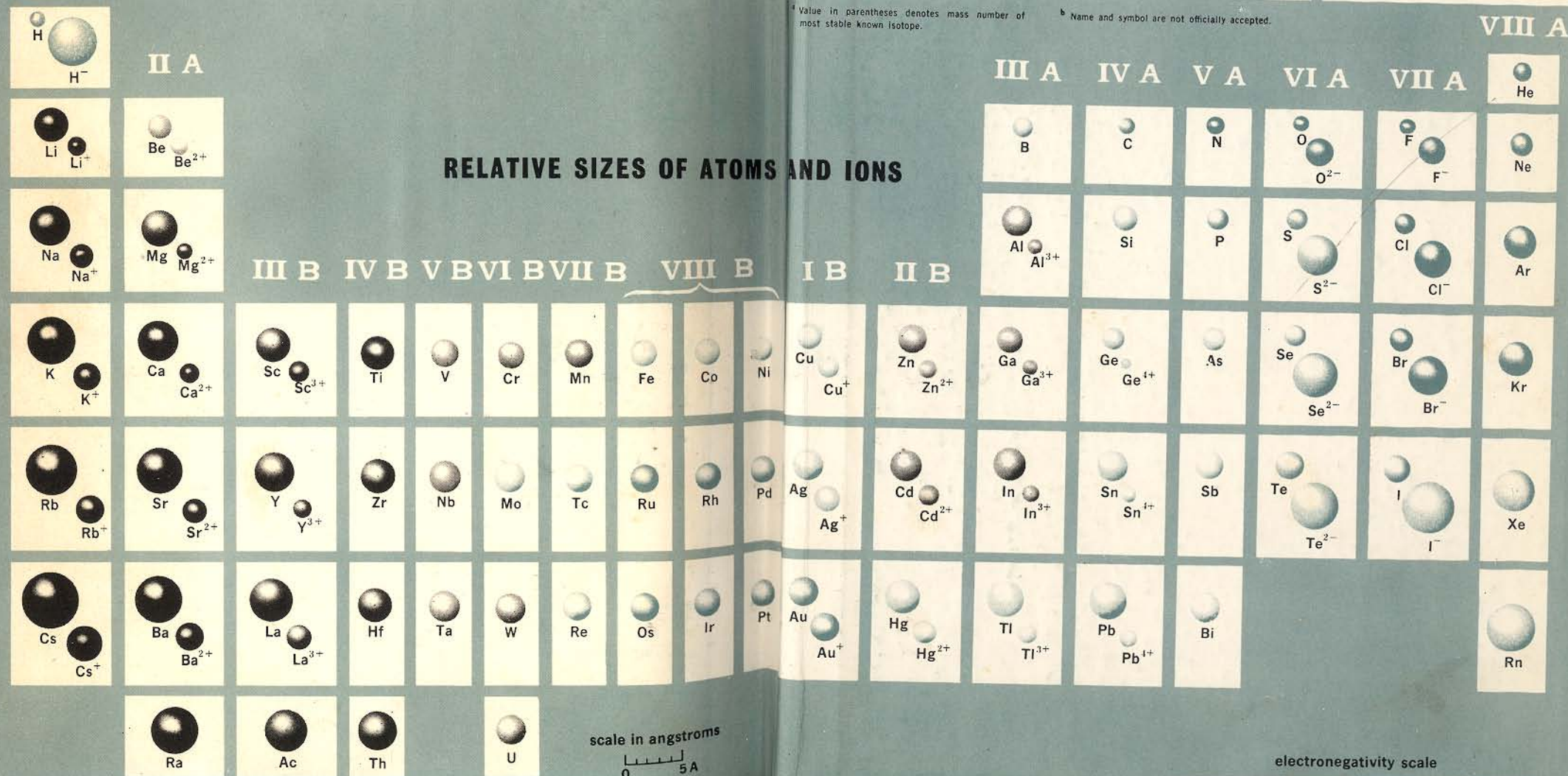
# INTERNATIONAL ATOMIC WEIGHTS 1961

element	symbol	atomic number	atomic weight <sup>a</sup>	element	symbol	atomic number	atomic weight <sup>a</sup>	element	symbol	atomic number	atomic weight <sup>a</sup>	element	symbol	atomic number	atomic weight <sup>a</sup>	element	symbol	atomic number	atomic weight <sup>a</sup>
actinium	Ac	89	(227)	cobalt	Co	27	58.9332	iron	Fe	26	55.847	palladium	Pd	46	106.4	strontium	Sr	38	87.62
aluminum	Al	13	26.9815	copper	Cu	29	63.54	krypton	Kr	36	83.80	phosphorus	P	15	30.9738	sulfur	S	16	32.064
americium	Am	95	(243)	curium	Cm	96	(247)	lanthanum	La	57	138.91	platinum	Pt	78	195.09	tantalum	Ta	73	180.948
antimony	Sb	51	121.75	dysprosium	Dy	68	162.50	lawrencium	Lr	103	(257)	plutonium	Pu	94	(244)	technetium	Tc	43	(99)
argon	Ar	18	39.948	einsteinium	Es	99	(254)	lead	Pb	82	207.19	polonium	Po	84	(210)	tellurium	Te	52	127.60
arsenic	As	33	74.9216	erbium	Er	68	167.26	lithium	Li	3	6.939	potassium	K	19	39.102	thorium	Th	90	232.038
astatine	At	85	(210)	europtium	Eu	63	151.96	lutetium	Lu	71	174.97	praseodymium	Pr	59	140.907	thulium	Tm	69	168.934
barium	Ba	56	137.34	fermium	Fm	100	(253)	magnesium	Mg	12	24.312	promethium	Pm	61	(147)	tin	Sn	50	118.69
berkelium	Bk	97	(247)	fluorine	F	9	18.9984	manganese	Mn	25	54.9380	protactinium	Pa	91	(231)	titanium	Ti	22	47.90
beryllium	Be	4	9.0122	francium	Fr	87	(223)	mendelevium	Md	101	(256)	radium	Ra	88	(226)	tungsten	W	74	183.85
bismuth	Bi	83	208.980	gadolinium	Gd	64	157.25	mercury	Hg	80	200.59	radon	Rn	86	(222)	uranium	U	92	238.03
boron	B	5	10.811	gallium	Ga	31	69.72	molybdenum	Mo	42	95.94	rhenium	Re	75	186.2	vanadium	V	23	50.942
bromine	Br	35	79.909	germanium	Ge	32	72.59	neodymium	Nd	60	144.24	rhubidium	Rb	37	85.47	xenon	Xe	54	131.30
cadmium	Cd	48	112.40	gold	Au	79	196.967	neon	Ne	10	20.183	ruthenium	Ru	44	101.07	ytterbium	Yb	70	173.04
calcium	Ca	20	40.08	hafnium	Hf	72	178.49	neptunium	Np	93	(237)	samarium	Sm	62	150.35	yttrium	Y	39	88.905
californium	Cf	98	(249)	helium	He	2	4.0026	nickel	Ni	28	58.71	scandium	Sc	21	44.956	zinc	Zn	30	65.37
carbon	C	6	12.01115	holmium	Ho	67	164.930	niobium	Nb	41	92.906	silicon	Si	14	28.086	zirconium	Zr	40	91.22
cerium	Ce	58	140.12	hydrogen	H	1	1.00794	nitrogen	N	7	14.0067	sodium	Na	11	22.9898				
cesium	Cs	55	132.905	iodine	I	53	126.9044	nobelium <sup>b</sup>	No	102	(256)								
chlorine	Cl	17	35.453	iridium	Ir	77	192.2	osmium	Os	76	190.2								
chromium	Cr	24	51.998					oxygen	O	8	15.9994								

<sup>a</sup> Value in parentheses denotes mass number of most stable known isotope.

<sup>b</sup> Name and symbol are not officially accepted.

## RELATIVE SIZES OF ATOMS AND IONS





KEENAN  
AND  
WOOD

GENERAL COLLEGE  
CHEMISTRY

HARPER &  
ROW  
WEATHER-  
HILL